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SPINACH AND BEETROOT EXTRACTS AS SENSITIZERS FOR ZnO BASED DSSC

Aakash Umesh Bhanushali, Ali Asgar Parsola , Sachin Yadav, R. Pratibha Nalini
B.Tech, School of Mechanical and Building Sciences ,VIT Chennai
Asst. Professor, School of Mechanical and Building Sciences, VIT Chennai

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ABSTRACT
One of the attractive solutions to third generation photovoltaic approach is to move towards hybrid optoelectronic systems such as Dye Sensitized Solar Cells (DSSCs) which consists of an inorganic-organic hybrid structures. The possibility of achieving sensitization effect from natural dyes is beneficial in terms of biodegradability and cost-effectiveness. In this context, this paper aims to study the extraction process of the natural dyes and its absorption characteristics. The study is carried out on extracts taken out using a very simple approach from beetroot, spinach and a mixture of both. The feasibility of using these dyes on a ZnO based DSSC prototype is investigated.

INTRODUCTION
Utilization of the solar energy generated from sun and conversion into the electrical energy is the most important technology for future green energy [1]. Dye sensitized solar cells (DSSC) is one such attractive concept developed by Michael Gratzel [2]. DSSCs with combination of the nanostructured thin films emerged as a new class of low cost solar cells. The operation of DSSCs depends to a large extent upon the dye that is used as a sensitizer. One of the important dye which was introduced in 1991 for DSSCs by O'Regan and Gratzel [2] was Ruthenium dye. The efficiency of the Gratzel DSSC was obtained 7 %. In 1993, the efficiency of the DSSC based on ruthenium dye increased to 10.3 % [3] and presently efficiencies upto 11% can be obtained [4]. But, the cost of the ruthenium dye is high [5] and hence the commercialization of the DSSCs with the stability issues and efficiency issues turns out to be difficult. In addition, the artificial and various synthetic dyes usually used comprise of heavy metals and thus pose an environmental degradation threat. Therefore natural dyes are considered as a viable option as it gives a dual benefit of being eco-friendly and less expensive. This is promising in reducing the overall cost of DSSCs.

Green leaves contain chlorophyll which gives it the ability to do the photosynthesis process using the solar energy. A mimicking of this process termed as "Artificial photosynthesis" has been the backbone of a recent type of solar cells based on this effect [6]. Various natural dyes from plants were used as sensitizers in DSSCs such as teak (Tectona grandis), tamarind (Tamarindus indica), eucalyptus (Eucalyptus globulus), the flower of crimson bottle brush (Callistemon citrinus) [7], Alkanna tinctoria plant seeds (Tausch) [8], anethum graveolens, parsley, arugula leaves [9], P. sativa and B. vulgar [10], flowers of the Rhododendron species [11], siahkooti fruit [12], lawsonia inermis seeds [13]. The important advantage of the natural dyes over a synthetic dye is that the extraction process is simple. Moreover, sufficient absorption coefficients are obtained from natural dyes also and hence it can act as a good sensitizer [14]. Chlorophyll has the ability to absorb light in the range of 453 and 662 nm [15] and obtains its colour by reflecting the green colour wavelength. Betalain absorb the radiation in the range of 476 and 600 nm [16] and obtain its colour by reflecting red colour wavelength. Belatin also can be used as sensitizer for DSSCs which can be extracted from beetroot (Beta vulgaris).

The aim of this paper is to use a simple kitchen approach to extract the natural dyes from beetroot and spinach without going to sub-zero remperatures. The absorption property of the dye samples are investigated for their absorption behaviour, stability and band-gap properties individually and as mixtures. Dyes such as those used in this paper have also been reported using various extraction methods [17][18] and most of these involve a sub-zero temperature process. ZnO and TiO_2 is an interesting nanostructure for DSSC application due to its wide bandgap of around 3.37 eV [18] and 3.2 eV [19] respectively. ZnO nanostructures offer a varied morphology such as nano rods [20], nano needles [21], saws [22] and tetrapods [23] etc and hence offer better tailorability of bandgap. The feasibility of using the most optimized natural dye for a ZnO based DSSC prototype is explored.

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EXPERIMENTAL

Extraction of the chlorophyll dyes

Chlorophyll dye is extracted from Spinach leaves (Spinacia oleracea) using a simple room temperature approach. The fresh Spinach leaves were washed using distilled water and then cut into smaller pieces. The pieces were then dried at 75°C for 1 hour to remove the moisture content. After cooling to room temperature, the leaves were ground. The ground mixture were taken into the pan and heated at medium flame until the green thick layer start forming at the top of the mixture. The mixture was then allowed to cool down and filtered using a dry cloth. The resulting green coloured particle is pure chlorophyll at the top of the cloth. This is taken into the beaker and stored in the ethanol for further use (Fig. 1a) [24].

Extraction of the betalain dyes

Betalain dye which also is used as a sensitizer is extracted from Beetroot (Beta vulgaris). For dye extraction, the fresh beetroot was washed using distilled water, subjected to a heat treatment and subjected to process similar to the one reported above. This was also stored in ethanol for further use (Fig. 1b) [24].

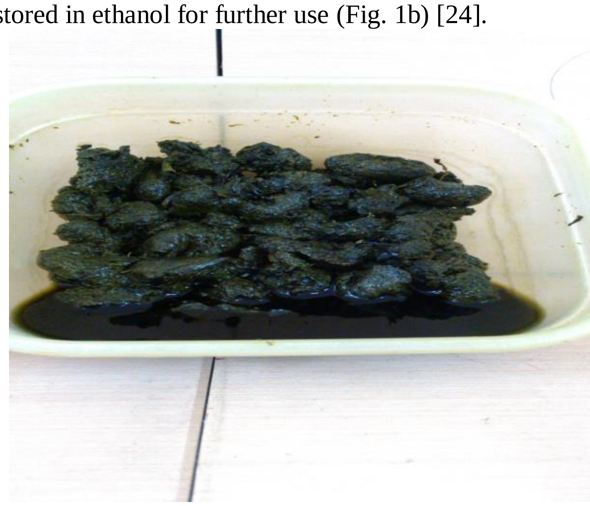

Fig 1 a) Dye extraction from Spinach.

Fig 1 b) Dye extraction from Beetroot.

Preparation of mixed dye

A mix of spinach and beetroot dye extracts is also prepared for comparison with the individually obtained dyes. For this purpose, 1:1 solution of the natural extracted dyes are taken into the beaker and mixed thoroughly. The

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resulting solution was dried at 75°C for 1 hour to remove the moisture content present and allowed to cool down to room temperature. The resulting mixture was stored in ethanol for further use after uniform mixing procedures (Fig. 2).

Fig. 2 Mixture of chlorophyll and betalain dyes.

All the three samples were subjected to UV-Visible absorption studies using the UV-Vis spectroscopy from Thermo Scientific Evolution 300 between 200-800 nm. The measurement was repeated in order to see the stability effect of dye. The bandgap was estimated in order to check the feasibility of using this dye for DSSC applications.

RESULTS AND DISCUSSIONS

Absorption studies

The UV-Vis absorption of extracted dye diluted in the ethanol was measured using UV-Visible spectroscopy, and is shown in Fig. 3. In the natural dyes extracted from spinach and beetroot, ethanol was used as a solvent. As can be noticed from the figure, in the spinach sample, there are two maxima: one in the range of 300 – 400 nm and another between 650-700nm. This is well in agreement of standard spectrum recorded from 'chlorophyll a' [25]. Whereas, in beetroot extract there is only one maxima in the range between 400-500nm. This is well agreement the presence of the betalain [26].

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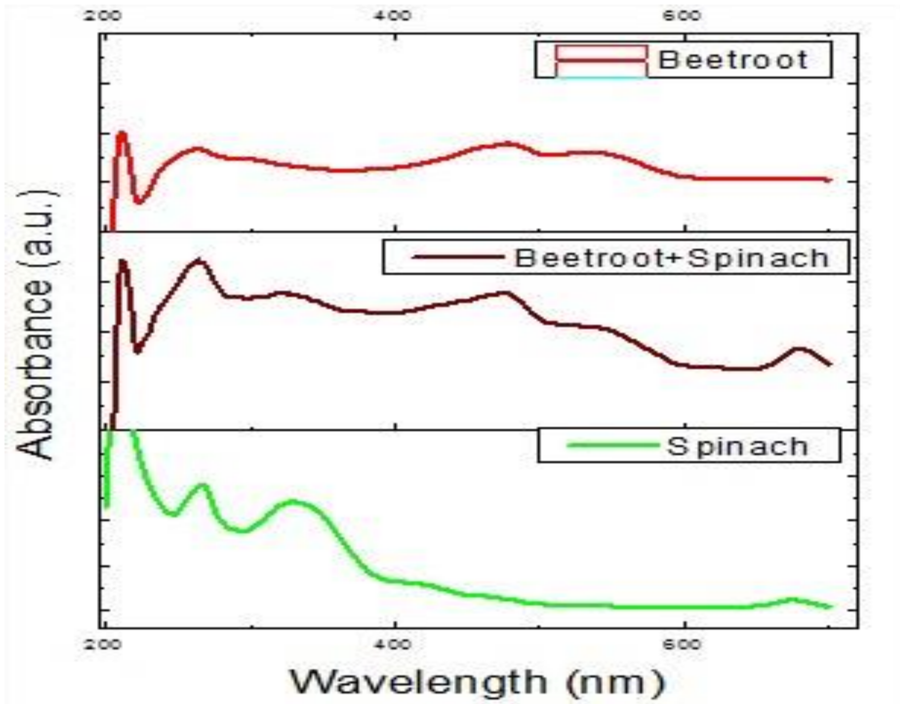

Fig. 3 Optical absorption results of natural dyes diluted in ethanol.

The mixed dye shows two absorption maxima, one in the range of 450 to 500 nm and another in the range between 650 to 700 nm. This is due to the combined contribution of the two dye pigments viz. Chlorophyll from spinach and betalain from beetroot.

3.2 Bandgap estimation

The bandgaps of the dye extracts are estimated from the absorption studies using Equation 1 and is tabulated in Table.1.

$$\Delta E = hc/\lambda$$

(Equation 1) Where, ΔE = Band gap (eV) , h = plank's constant = 6.626176 x 10^{-34} joule-seconds, c = speed of light = 3 x 10^{8} m/s, λ = wavelength of light (nm).

Sample	Bandgap (eV)
Spinach	3.14
Beetroot	2.48
Spinach + Beetroot	2.45

Table 1. Bandgap values for Spinach, Beetroot and Mix dye respectively.

The bandgap values obtained from the spinach extract and beetroot extract are comparable to those reported in literatures [27,28]. This confirms the successful extraction of the dyes with the presence of chlorophyll and belatin pigments suitable enough for DSSC application

DSSC prototype

As noticed from the absorption results above, the spinach dye extract gives a higher absorption and hence the feasibility of using this dye in a DSSC proptotype was explored. The DSSC prototype is made with ZnO as photoanode coated using the doctor's blade technique and carbon soot as the counter electrode on ITO substrate. A simple preliminary voltage test under normal room illumination recorded 300 mV stable output.

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Conclusion

The experiments conducted in this study is a preliminary step taken towards achieving a biodegradable eco-friendly and cost effective DSSCs that can be used for applications that does not require a high output. This work reports successful extraction of the natural dyes using a simple kitchen approach at nominal temperatures. The bandgaps of the chlorophyll and betalain dyes obtained from spinach and beetroot extracts are 3.14 eV and 2.48 eV respectively. The bandgap of the mix dyes is obtained as 2.45 eV. These values match well with the wide bandgap semiconductors traditionally used as photoanode for DSSCs. A DSSC device prototype made with spinach dye extract under normal illumination shows a stable output of 300mV rendering it promising for future device implementation.

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