Fabrication of Low Cost, Natural Dye-Sensitized Solar Cells (DSSCs)

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***Abstract* - Production of Dye Sensitized Solar Cells (DSSC) has been a topic of significant research in the recent past because of their fundamental scientific importance in the area of energy conversion. Ease of fabrication with commonly available materials, coupled with reasonable efficiency, has made DSSCs promising candidates in the production of low-cost solar cells. In this work, use of five natural dyes as photosensitizers for the production of dye-sensitized solar cells (DSSCs) is being reported. Advantages of employing natural dyes as photosensitizers in DSSC are due to their large absorption coefficients in visible range of light spectrum, relative abundance, ease of preparation and environmental friendliness. Furthermore, the production of natural dye based DSSCs is cost effective. DSSCs were fabricated using TiO2 as a semiconducting layer deposited on transparent fluorine-doped tin oxide (FTO) conductive glass. The absorption spectra of the natural dyes were analysed in the range of 450 - 670 nm. The resistance and voltages were recorded under various light conditions and the efficiency of natural dyes as photosensitizers was compared and discussed.**

***Index Terms* - Dye Sensitized Solar Cells (DSSCs); Renewable energy; Light harvesting pigments; Photosensitizers.**

I.INTRODUCTION

World over there is an ever-increasing demand of energy, coinciding with the depletion of readily accessible fossil fuels. Search for alternative energy sources, particularly renewable solar energy, has, therefore, become vital. Despite the clear advantages associated with the adoption of solar cells, they need to be cost-effective in comparison to conventional energy resources. Ever since significant breakthrough reported by O'Regan and Gratzel (1991) [1], dye sensitized solar cells (DSSCs) have gained considerable attention in research [2]. DSSCs are semiconductor devices which operate based on the conversion of solar radiation into electrical energy (Fig.1). They consist of 1. A transparent conducting oxide (TCO), usually comprising of fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO). 2. A mesoporous metal oxide layer which acts as a photoanode, usually developed from TiO_2 nanoparticles. 3. Sensitizer (dye molecules) anchored on to photoanode. 4. Electrolyte, mostly iodide/triiodide, that undergoes redox reactions. 5. A counter electrode, generally a glass, coated with platinum or graphite.

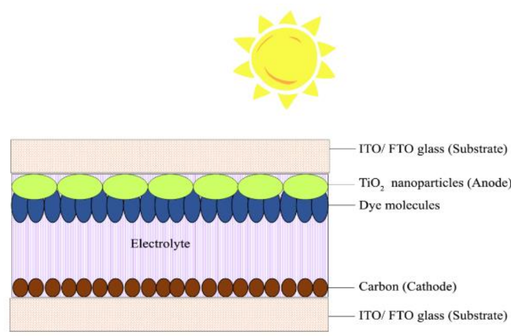


Fig 1. : Design of a typical DSSC

The dye molecules adsorbed on the surface of mesoporous TiO_2 layer, absorb incident photons and get excited. The excited dye molecules inject electrons into the conduction band of the mesoporous photoanode network and the dye molecules loose an electron and get oxidized. These injected electrons travel through the TiO_2 layer to the external load to reach counter electrode (CE). Electrons are then transferred to the electrolyte where the oxidized dye receives electrons from iodide ions (I^-) to replace the lost electrons and simultaneously the iodide molecules get oxidized to triiodide ions (I^{3-}). The electrolyte regenerates the dye [3]. Even though the iodide-tri iodide (I^- / I_3^-) electrolyte is very efficient, it suffers from a major drawback that it cannot be preserved. The electrolyte solution, if left outside, can dry out completely.

On the TiO_2 electrode (anode)

TiO_2–Dye+photon $\rightarrow TiO_2$–Dye* $\rightarrow$ e^- in TiO_2 and Dye^+

In the electrolyte solution

Dye+ + 2 I^- → {possible intermediate} → Dye + I_2^- ;

2 I_2^- → I^- + I_3^-

On the graphite-coated counter electrode (cathode)

I_3^- + 2 e^- → 3I^-

where, Dye* is the common notation used when an electron has absorbed a photon

The primary requirement for an efficient DSSC is the availability of a cost-effective sensitizer with efficient photon capturing ability over a broad range of visible light. The first DSSC developed was found to absorb visible light up to approximately 800 nm and exhibited energy conversion efficiency of about 7%. Recently, a conversion efficiency of 13% was reported by using mesoporous semiconductor electrodes and porphyrin sensitizers [4]. Photosensitizers comprise of a range of inorganic, organic or metal–organic dye molecules. The most successful sensitizers in terms of efficiency and stability are based on Ruthenium (Ru) bipyridyl compounds [5]. Use of synthetic organic dyes as photosensitizers in DSSCs provides better efficiency and high durability but they suffer from several limitations, such as high cost, tendency to undergo degradation, toxicity of materials, multi-step preparations and procedures, and time-consuming chromatographic methods [6,7,8]. Another critical component of DSSCs is Transparent Conductive glass which consists of a layer of conductive material on glass having about 20-30 Ω/sq resistance.

These limitations have opened up research activities to find alternate biocompatible/natural photosensitizers. Natural sensitizers contain plant pigments, such as anthocyanins, carotenoids, chlorophylls, and some others that exhibit the ability to absorb photons and inject charges to the conduction band of TiO_2, the semi-conductor component of DSSCs. Plant pigments can easily be extracted from fruits, flowers, leaves, seeds and bark, and can be used as sensitizers for DSSCs. Natural dyes/pigments exhibit large absorption coefficients in visible range of light, are relatively abundant, and their sample preparation is environment friendly. Moreover, the production of natural dye-based DSSC is cost effective. Keeping in view the properties and working of DSSC, the present work reports preparation of cells using economical and easily available materials and employing environment friendly options.

II. MATERIALS AND METHODS

Preparation of Transparent Conducting Oxide (TCO) glass *:* In view of the cost factor and non-availability of this conductive glass, we set out to imitate the properties of this glass by using minimum and easily available chemicals. The coating that is done on the glass is of ITO (Indium doped Tin Oxide) or of FTO (Fluorine doped Tin Oxide). In semiconductor production, doping is done to introduce impurities into a pure intrinsic semiconductor for the purpose of modulating its electrical properties. While making FTO glass, a substance with high fluoride content is required to react with Tin Oxide. Keeping this in mind, a layer of fluoride must be thoroughly spread on the glass and an oxidation reaction of chemical must take place on it to give a doped glass. Thus, we used the most easily accessible fluoride source, i.e commercially available toothpaste. Toothpaste generally has high fluoride content (~1000 ppm) as a major component for preventing tooth decay. Next, we used Tin(II) Chloride dihydrate ($SnCl_2.2H_2O$) (melting point is 37.7°C) which, upon prolonged heating, can attain a temperature of 400°C, resulting in the formation of Tin(II) Oxide (SnO_2). The reaction is : $2SnCl_2 + 2H_2O + O_2 \rightarrow 4HCl + 2SnO_2$

The solid tends to liquify upon heating and the vapors start sticking to the surface of the glass slide which already has a layer of fluoride on it. This produces a doped conductive glass slide, which is transparent and has a rainbow shine to it. One surface of the two transparent glass slides is evenly coated with toothpaste and dried for 5-8 min. Small amount of detergent is dissolved in 50 mL of water. Dry slides coated with toothpaste on one surface are gently washed with soapy water. Few drops of ethanol are poured on the slide and the layer so detached, is removed very carefully. The slides are damped dry using a tissue paper. Four spacers are placed on the corners of one of the slides. Solid $SnCl_2.2H_2O$ is spread evenly on the surface of fluoride-coated slide and the other slide is placed over the first. The slides are carefully placed on a wire gauze and are sintered for about 35-45 min. Slides are then cooled and the decomposed solid is removed using tissue paper. The shine on the slides can be easily observed. Using a multimeter, the resistance of the glass slides is checked. It should be at least 20-30 KΩ.

Preparation of Homogenized Titanium dioxide: Titanium dioxide suspension is prepared by gradually adding 10 mL of dilute acetic acid solution to 6 g TiO_2 (s), with constant stirring and grinding using a mortar and pestle until smooth and lump-free solution is formed. One drop of clear detergent is added, mixed lightly and left for 15 min. Surfactant treatment and grinding, help break up the nanoparticles.

Coating slides with Titanium dioxide: One of the TCO glass slides is tested using a multimeter to determine the conductive side. The slide is masked about 1 cm from one side using a scotch tape. Two or three drops of TiO_2 solution are dropped on to it and evenly spread immediately using another glass slide. The coating is allowed to dry for a few minutes before removing the tape. The slide is placed on a wire gauze and sintered for about 30-45 min. The coated slide initially turns yellow and then white again. It is allowed to slowly cool to room temperature. The resulting TiO_2 layer is nanoporous, which are only a few nanometers (10^{-9} m) wide. These coated slides can be stored at room temperature for later use.

Preparation of dye solutions: The below mentioned plant extracts were prepared in water (1 gm/1ml water):

1. Coffee dye solution : Since instant coffee powder is soluble in water, it is dissolved in distilled water and used as a dye solution.
2. Pomegranate dye solution : The pomegranate arils (the red seedy part) are crushed using a mortar and pestle or blended to acquire juice for usage as a dye solution .
3. Red Bougainvillea dye solution : The flowers are heated in water in a beaker with stirring in between using a glass rod. The resulting solution is filtered using a funnel.
4. Orange Marigold dye solution : Marigold flowers are picked and dissolved in water with stirring, filtered to obtain a dye solution.
5. Bitterleaf dye solution : Since bitter leaf does not loose its color readily, it is boiled carefully on addition of distilled water for a prolonged time and finally filter to get it's dye solution.

Staining of TiO_2 coated slides with dye solutions: Each dye solution is poured into a clean petri dish. The TiO_2 coated slides are placed upside down in the dye solution for about 15 min to stain thoroughly. The slides are rinsed with distilled water, followed by ethanol and blotted dry.

Carbon-coated counter electrode: The conductive side of each coated slide is determined using a multimeter. The slides are held using a pair of tongs and brought above a yellow flame till coating of the slide becomes black. The excessive coat can also be removed using a tissue.

Assembly of DSSC : The graphite -coated slides are placed face down on top of the dye stained TiO_2 coated side of the second slide. The slides are held together using a rubber band or binder clips. Using a dropper, 1-2 drops of liquid iodide-triiodide electrolyte solution are added to the crease between the two slides. The solution will be drawn into the cell by capillary action and will stain the entire inside of the slides. The alligator clips are then attached to the two overhanging edges of the slides, and the other to the multimeter with the negative terminal attached to the dye stained TiO_2 coated slide and the positive terminal attached to the graphite coated slide. The resistance and voltage are measured in room light illumination and in sunlight.

Preservation of cell : The cells so prepared can be preserved for some time in a dark bottle filled with acetic acid solution to maintain a pH of 3-4.

Calculation of λ_{max} of the dye solution : One of the cuvette is filled with distilled water and the other with dye solution suitably diluted with distilled water. Absorbance is recorded in the range of 450 to 670 nm (Figure 1).

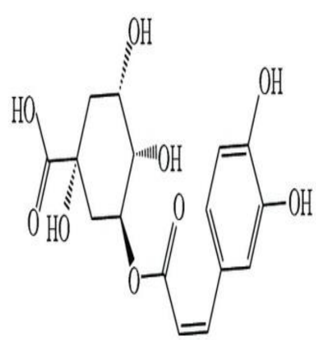
III. RESULTS AND DISCUSSION

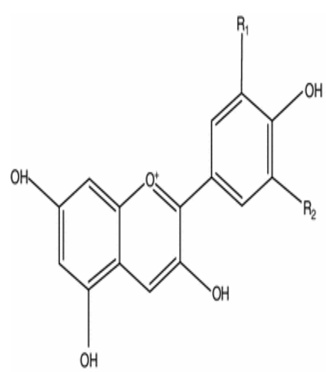
In the recent past, researchers have focused on the conversion of solar radiation into electric energy through devices known as photovoltaic devices or solar cells [9]. The first-generation solar cells consist of microcrystalline silicon solar cells, which are expensive and also temperature-sensitive . Dye sensitive solar cells (DSSCs) imitate plant's ability to harness solar energy. Use of natural dyes as sensitizers has advantages and disadvantages. The potential advantage is that organic molecules can undergo two electron, two proton redox change than a metal-centered dye which undergoes one electron redox chemistry. The disadvantage is that oxidation of organic compounds can be irreversible, which can be detrimental for the stability of DSSCs. Fabrication of solar cells with TiO2 is a critical factor that determines the photovoltaic properties of DSSCs. Indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO) proved significant in enhancing the efficiency of DSSCs [8,10]. The mesoporous layer of TiO_2 provides a surface for dye absorption and reaction site for light absorption, thereby enhancing dye-regeneration ability and light harvesting efficiency of DSSCs. These conditions cause a high short circuit current in DSSCs [11].

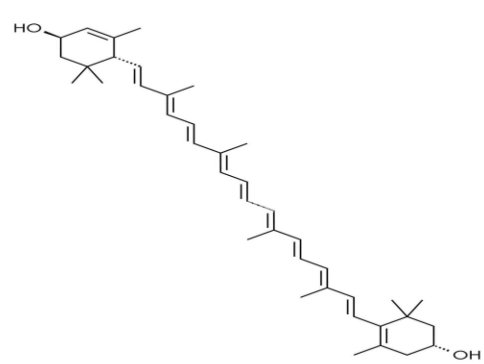
Pre-requisites for photosensitizers to function in DSSCs are their ability to absorb in visible and near-infrared regions of the solar spectrum and capacity to bind the semiconductor TiO_2. Several plant extracts have been shown to serve as efficient photosensitizers [12]. The photosensitizers belong to different chemical classes which mainly contain chlorophyll, anthocyanins, carotenoids, betacyanin or flavonoids. Stability of natural photosensitizers is, however, debatable. Anthocyanins and betacyanins have been reported to remain stable for more than one year when protected from direct sunlight [13].

Plants used in the present work contains following major pigments :chlorophylls, anthocyanins, betains, carotenoids**.** It is evident from Fig. 2 that the dyes chosen from plant sources belong to varied categories of phytochemicals and they have their unique patterns of absorbance in the visible range of spectrum (Fig. 3). It is, therefore, significant to compare their relative efficiencies as dye components of DSSCs. The dye solutions of the five types of plant extracts gave different results when tested in artificial light and in sunlight (Table 1). The cells were observed to give increasing values of voltage on increasing the illumination. The cells performed even in very low light and showed satisfactory results. The best performance of cells was evident by pomegranate as the dye source which contained anthocyanins. These molecules have carbonyl and hydroxyl groups bound to the surface of TiO_2 semiconductor, which help in excitation and transfer of electrons from anthocyanin molecules to the conduction band of the porous TiO_2 film. Other types of plant pigments/dyes, such as chlorophyll, betain and carotenoids, are relatively less efficient as compared to anthocyanins. The structure and bonding made by these pigment molecules with TiO_2 surface can be analyzed in detail in future work, in order to obtain better yields and stability similar that of anthocyanin molecules.

Source: Coffee Pomegranate Orange marigold

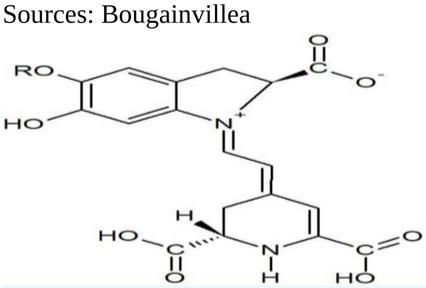


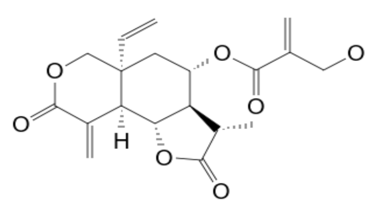




Dyes present: Chlorogenic acid Anthocyanins Leutin

Sources: Bougainvillea Bitterleaf





Dyes present: Betacyanin Vernodalin

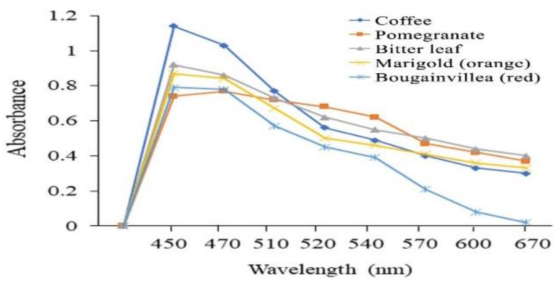


Fig. 2 Structure of dyes from plant/plant parts used in present work for DSSC fabrication

Fig. 3 Absorbance patterns of plants pigments.

TABLE I Resistance and voltage of five DSSCs tested in various light conditions

SOURCE OF DYE	DYE	λ_{max} (nm)	ROOM LIGHT (kΩ,mV)	UNDER ILLUMINATION (kΩ,mV)	SUNLIGHT (kΩ,mV)	CONDITIONS
COFFEE	Anthraquinone	450	R = 2.246	R = 3.070	R = 16.390	14°C
			V = 50.8	V = 85.3	V = 164.0	
POMEGRANATE	Anthocyanin	470	R = 178.7	R = 360.4	R = 292.9	Cloudy day,11°C
			V= 90.4	V = 172.3	V = 250.5	
RED BOUGAINVILLEA	Betalain	450	R = 129.6	R = 215.5	R = 240.7	15°C
			V = 79.4	V = 107.1	V = 130.3	
ORANGE MARIGOLD	Carotenoid	450	R = 170.4	R = 109.5	R = 186.5	12°C
			V =42.5	V = 50.9	V = 72.0	
BITTERLEAF	Chlorophyll	450	R =183.1	R = 127.9	R = 190.4	12°C
			V= 43.3	V = 64.7	V = 125.4	

Anthocyanins are flavonoid pigments possessing variable colors, depending on structure. They absorb excess radiation in plants, thereby minimizing oxidative damage [14]. It is this unique feature of anthocyanins which dominates other phytochemicals in determining their role as effective dyes in low-cost fabrication of DSSCs. Anthocyanins are non-photochemical pigments and in plants their synthesis is closely related to flavonoid metabolism [15]. Co-pigmentation reaction of anthocyanins with other compounds generally enhances and stabilizes them by blocking the hydration of chromophore and hyperchromic effect or bathochromic shift in absorption spectra. Phytochemicals, such as flavonoids, alkaloids, amino acids and metallic ions, have the potential to bind anthocyanins [16]. The anthocyanin charging-transfer mechanism in DSSCs is ligand centric due to the presence of TiO_2 complexing at O and OH sites. The chemical absorption of anthocyanin is due to their alcohol-bound proton condensing with hydroxyl groups present on TiO_2 film surface. Charge density of anthocyanin increases after complexing with Ti^{4+} and allows electronic coupling for charge injection[16]. Anthocyanins exhibit a broad band absorption spectrum ranging from 450-580 nm, which is sensitive to pH. Compared to the absorption of free forms of anthocyanins, their absorption spectra shift to longer or shorter wavelengths upon binding with TiO_2 film surface. This is likely be due to metal s competing with protons that displace them.

IV. CONCLUSIONS

Assmbly of DSSCs suggested in the present work is economical, and easy to construct from abundantly available and stable plant-based resource materials. DSSCs can work effectively with natural dyes. They work even in low-light conditions, such as indirect sunlight and in cloudy skies. Best results are obtained from pomegranate which contains antocyanins. These DSSCs are environmentally friendly. Even though the iodide-tri iodide (I^-/I_3^-) electrolyte is very efficient, it suffers from a major drawback that it does not get preserved. The electrolyte solution if left outside, dries out. Plant dyes degrade when exposed to UV radiations in combination with oxygen. Preferably, a UV protection film or UV absorbing luminescent chromophores may be used outside the anode. Liquid electrolyte requires an appropriate encapsulation against leakage. Use of solid-state electrolyte can improve the stability DSSCs. Despite these challenges, DSSC assembly is a promising technology and there are many opportunities for further development in regard to the repeatability and reliability of natural dyes as well as all other components employed in DSSC for the purpose of commercialization.

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