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DIRECT CONVERSION OF SOLAR ENERGY TO ELECTRIC ENERGY

Investigation of Some Common Fijian Flower Dyes as Photosensi-Tizers for dye Sensitized Solar Cellsabstract[1]

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Abstract—Dye sensitized solar cells (DSSC) were fabricated using *Allamanda cathartic*, *Bougainvillea spectabilis* and *Cosmos sulphureus* dyes obtained from local Fijian flowers. The photoanodes were made from electro-phoretiaclly grown *Titanium dioxide* films coated with dyes. DSSCs with *Cosmos sulphureus* exhibited the best efficiency of 0.54% followed by *Allamanda cathartic* (0.40%) and *Bougainvillea spectabilis* (0.38%). The photoaction spectra of these cells were also studied.

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INTRODUCTION

A dye sensitized solar cell (DSSC) has been defined as a "molecular machine that is one of the first devices to go beyond microelectronics technology into the realm of what is known as nanotechnology" [1]. It is a third generation photovoltaic device that holds significant promise for the inexpensive conversion for solar energy into electrical energy. DSSC or so-called Gratzel cell was invented in 1991 at the laboratory of Photonics and Interfaces in the Ecole Polytechnique Federale de Lausanne, Switzerland by the successful combination of nanostructured electrodes and efficient charge injection dyes [2].

DSSC converts solar energy into electricity based on the sensitization of wide bandgap semiconductors by organic dyes and basically comprises a photoelectrode, redox electrolyte and a counter electrode. It mimics natural photosynthesis process in the use of a dye as the light harvester to produce excited electrons with titanium dioxide (TiO_2) replacing carbon dioxide as the electron acceptor, iodide and triiodide replacing water and oxygen as the electron donor and oxidation product, and a multilayer structure (similar to thylakoid membrane) to enhance both the light absorption and conversion efficiency (η) [3]. Nanocrystalline TiO_2 is mesoporous, stable and has a suitable wide bandgap for this application [4].

The best photovoltaic performance in terms of both conversion yield and long-term stability has so far been achieved with complexes of ruthenium (Ru). However, the use of Ru derived from relatively scarce natural resources and its long-term unavailability is doubtful [5]. It is possible to use natural dyes as photosensitizers in the place of expensive dyes albeit with much lower efficiencies. Their advantages over organic dyes include easy availability, abundance, require simple extraction method, can be applied without further purification, are environmentally friendly and considerably reduce the cost of devices [6–8].

This work presents our investigation on natural flower photosensitizers available locally, regarding their sensitization activity in DSSCs. We have studied performance of various natural-dyes coated elec-tro-chemically grown TiO_2 based DSSCs.

EXPERIMENTAL

Preparation of TiO_2 Films

TiO_2 films were prepared by electrophoretic deposition (EPD). TEC 15 conducting glass plates (Dyesol—25.00 mm × 25.00 mm × 2.27 mm) and aluminium (Al) plates (50.00 mm × 35.00 mm × 2.62 mm) were used as the cathode and anode, respectively. The plates were placed parallel to each other in a beaker containing the $TiO|_2$ suspension, as shown in Fig. 1. 0.05 g of anatase TiO_2 was added to a solution of 0.04 g of 12 and 5 mL of acetylacetone (dispersing agents) to prepare the suspension. To achieve a homogeneous

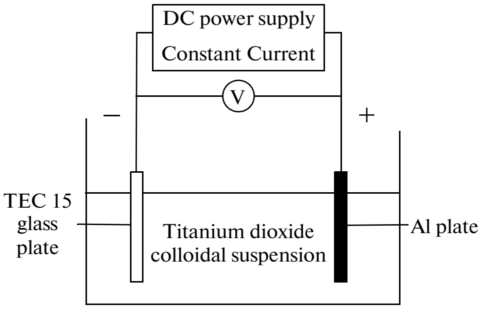

Fig. 1. Schematic diagram for constant current method EPD.

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suspension, it was sonicated and magnetically stirred for 30 mins. AI plates were washed with acetone before use [9]. The distance separating the anode and cathode was fixed at 10 mm [4].

Constant current EPD method was applied whereby the electrophoresis current densities were kept at 0.15 mA cm^{-2} and deposition duration was maintained at 30 s.

After performing EPD, the as-grown films were annealed in an oven at 250°C for 1 h. Annealing evaporated residual water and improved TiO_2 nanoparticle connection to the glass surface [10].

Extraction of Dyes

Dyes from fresh golden trumpet (*Allamanda cathartic*), bougainvillea (*Bougainvillea spectabilis*) and cosmos (*Cosmos sulphureus/Sulfur Cosmos*) flowers were extracted in methanol and solid residues were filtered out to obtain clear dye solutions. TiO_2 coated films prepared by EPD were immersed in the dye solutions for approximately half an hour. The non-adsorbed dye was washed off first in distilled water, followed by ethanol and the stained TiO_2 film was allowed to dry in air.

Assembly of DSSC

Platinum (Pt) coated TEC electrodes (Dyesol) were used as counter electrodes. DSSCs were assembled by placing the counter electrode on top so that the conductive side of the counter electrode faced the stained TiO_2 film. The iodide electrolyte, Iodolyte AN–50 (Solaronix) was introduced in between the two electrodes. The electrolyte fills the space between the electrodes by capillary action. Any excess electrolyte was removed from the edges of the cell with a paper dampened with acetone. Sealing material SX1170–25PF was used to prevent leakage and evaporation of the electrolyte. Sealing also prevents moisture from entering, which can result in degradation of cell components if water penetrates in.

CHARACTERIZATION AND MEASUREMENT

The absorption spectra of the dye solutions and the dyes stained TiO_2 films were recorded using a Lamda 25 UV–VIS spectrophotometer. The dye solutions were diluted by a factor of 10 for absorption measurements [3]. The adsorption amount of dye on TiO_2 film was evaluated from the concentration of dye in a mixed solution of 0.1 MNaOH and ethanol at a volume ratio 1:1 [10].

To investigate spectral response, cells were illuminated using a lamp and corresponding short circuit current (I_{sc}) values were measured using filters of different wavelengths. Intensities at different wavelengths were measured and the normalized short circuit current density (J_{sc}) was calculated.

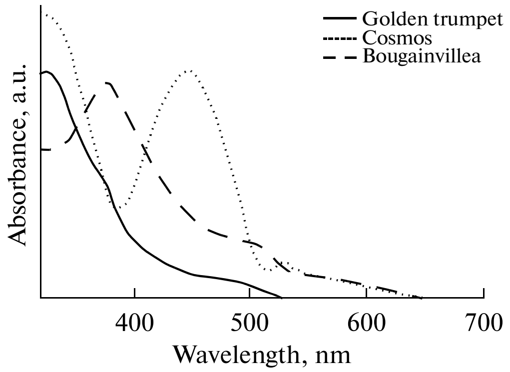

Fig. 2. Absorption spectra for golden trumpet, cosmos and bougainvillea dye extracts.

RESULTS AND DISCUSSION

UV–VIS Spectrum

Flavonoids, a group of secondary metabolites belonging to the class of phenylpropanoids, have the widest color range, from pale-yellow to blue. In particular, anthocyanins, a class of flavonoids, are responsible for the orange to- blue colors found in many flowers, leaves, fruits, seeds and other tissues. They are widely distributed in seed plants, are water-soluble, and are stored in vacuoles. Betalains, yellow-to-red nitrogen-containing compounds, are derived from tyrosine. They are also water-soluble and stored in vacuoles, but are found only in the order Caryophyllales. Carotenoids, which are isoprenoids are found ubiquitously in plants and microorganisms. They are essential components of photosystems and confer yellow-to-red coloration to flowers and fruits. Flavonoids/anthocyanins and carotenoids are often present in the same organs, and their combination increases color variety [11].

The flower dyes were soluble in methanol and resulted in light yellow color for golden trumpet, magenta for bougainvillea and deep yellow for cosmos, respectively. The fastest absorption rate was observed for cosmos, followed by bougainvillea and golden trumpet. Figure 2 portrays the absorption spectra of golden trumpet, bougainvillea and cosmos flowers.

Compounds are colored because they absorb light in the visible region of the spectrum that is between 400 and 800 nm. Light absorption in this region and in UV (150 to 400 nm) causes the excitation of electrons in the molecule, and the more firmly the electrons are bound, the higher will be the energy needed, that is, the shorter will be the wavelength at which the light is absorbed. Thus, compounds containing double and triple bond with no non-bonded electrons show absorption at much higher wavelengths. Absorption peak of golden trumpet, bougainvillea and cosmos occurred at 325, 383 and 442 nm, respectively. This is due to various types of flower pigments and the colors of the dye solutions. It is also essential for the sensitizer

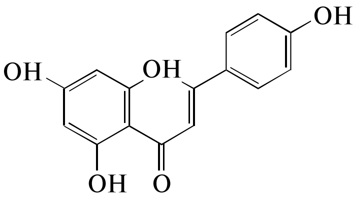

Fig. 3. Structure of chalcine.

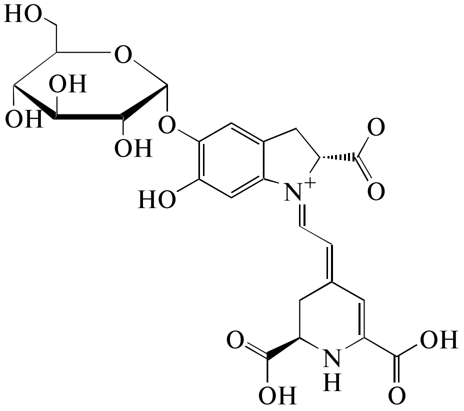

Fig. 4. Structure of betanin.

dye to have enough energy levels to transfer electrons and anchor groups to have affinity for semiconductors, TiO_2 in this case.

The main coloring agent in *Cosmos sulphureus* is a pentahydroxy chalcone hexoside, an anthochlorine type flavonoid generically known as coreopsin. However, coloring is also provided by additional flavonoids in the plant, such as isoquercitin and the luteolin glycosides (golden yellow). Chalcones constitute minor family of substances belonging to the flavonoids. They are highly reactive substances of a varied nature and they experience chemical and physical transformations. Chalcones belong to a class of α, β-unsaturated aromatic ketones (Fig. 3) responsible for the antimicrobial activity, which occurs abundantly in nature, especially in plants [12].

Bougainville (*Bougainvillea spectabilis*) is a tropical, shrubby vine whose flower bracts color is because of betalains, specifically the compound betanin [13]. Betalains are water-soluble vacuolar yellow and violet pigments and are known as nitrogenous anthocyanin and chromo-alkaloids due to the presence of a nitrogen atom in the chromo-phore [14]. The advantage of betalain color is that the color does not depend on the pH and is more stable than that from anthocyanins [11].

Allamanda cathartica also known as yellow bell, golden trumpet or buttercup flower has carotenoid pigment. Carotenoids provide many fruits and flowers with distinctive red, orange and yellow color. They are a large family of isoprenoids and their distinctive colors are due to a series of conjugated double bonds [14]. According to [15], the main carotenoid found in *Allamanda cathartica* is lutein.

A requirement of a suitable DSSC dye is that it should possess several =O or –OH groups capable of chelating to the Ti(lV) sites on the TiO_2 surface [16]. Adsorption of flavonoid to the surface of TiO_2 is a rapid reaction, displacing an OH^- counterion form the Ti(IV) site that combines with a proton donated by the flavonoid structure. For the DSSC to be efficient, the solar absorptivity should be strong. Furthermore, injection should be efficient such as the sensitizing dye must inject electrons quickly, with few competing excited-state decay processes, so that injection is the preferred de-excitation route. Additionally, recombination and recapture of injected electrons before they can be collected at the back contact must be slow [3]. Normally, flavonoids and their derivates show a broad absorption band in the range of visible light ascribed to charge transfer transitions from highest occupies orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) [7]. Fig. 6 shows adsorption characteristics of the respective dye solutions on the TiO_2 surface.

After immersion of the coated TiO_2 in the NaOH and ethanol mixture, the dye was de-absorbed and the solution was further analyzed. The peaks of the adsorbed solution shifted to 379, 542 and 458 nm for golden trumpet, bougainvillea and cosmos, respectively. Upon adsorption of the dye extracts from the TiO_2 films, the visible absorption band shifts to higher energy [7]. This difference in peak is due to the ability of the chalcone, betanin and lutein pigment to bond with TiO_2.

Adsorption of dye to the semiconductor TiO_2 surface is a quick reaction, forming a very strong complex showing prevalently the quinonodial form. Chalcone, betalain and lutein pigments possess –OH group veri-

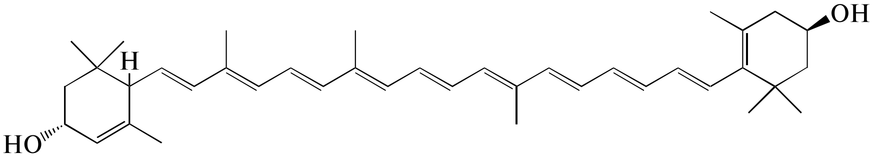

Fig. 5. Structure of lutein.

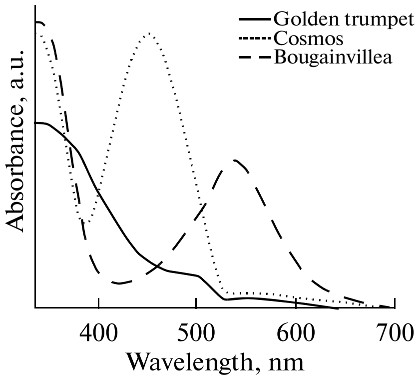

Fig. 6. Adsorption spectra for golden trumpet, cosmos and bougainvillea dye extracts on TiO_2.

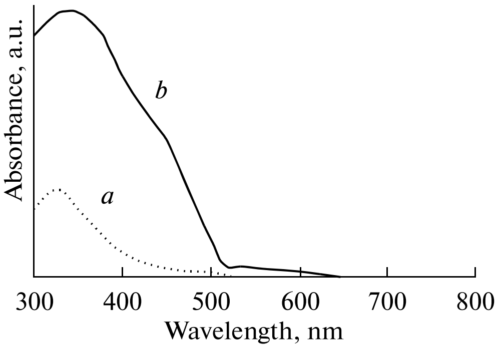

Fig. 7. Light absorption spectra of (*a*) golden trumpet dye solution and (*b*) golden trumpet adsorbed on TiO_2.

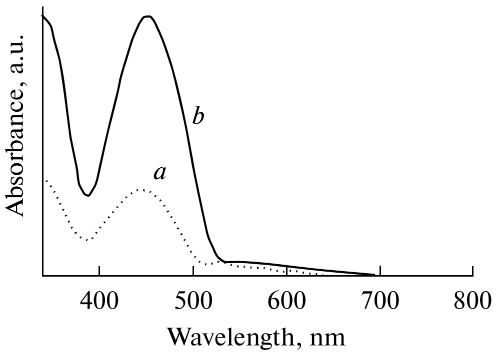

Fig. 8. Light absorption spectra of (*a*) cosmos dye solution and (*b*) cosmos adsorbed on TiO_2.

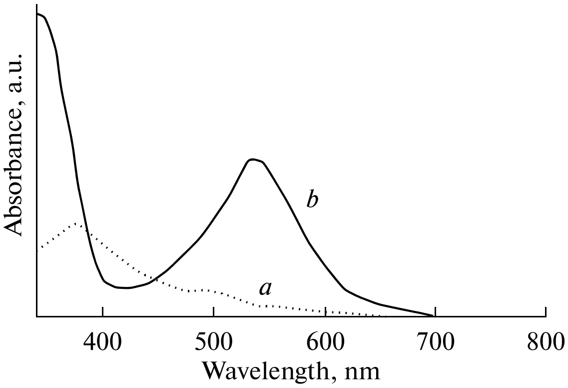

Fig. 9. Light absorption spectra of (*a*) bougainvillea dye solution and (*b*) bougainvillea adsorbed on TiO_2.

fying the chelating mechanism of the dye to the TiO_2 particles. This chemical reaction is a result of alcoholic bound protons which condense with the hydroxyl groups present at the surface of nanostructured TiO_2 film with the contribution of the chelating effect due to the nearest hydroxyl group towards Ti(IV) sites on the semiconductor nanocrystalline layer [7]. It is generally accepted that the chemical adsorption of dyes take place due to condensation of the alcoholic bound protons with the hydroxyl groups in the surface of nanostructured TiO_2. Hence this chemical attachment affects the energy levels of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the pigments, which eventually affect the bandgap of these materials and a shift in the absorption spectra. Figures 7–9 show the absorption and adsorption characteristics of the golden trumpet, cosmos and bougainvillea.

In case of golden trumpet, a positive shift in the absorption peak was observed after adsorption. Lutein pigment showed a broader absorption peak as compared to betanin and chalcone. The peak shifted from 325 to 458 nm while bougainvillea produced the widest shift from 383 to 542 nm. Chalcone in cosmos provided a shift of 442 to 458 nm. This shift is due to the extent of the binding of molecule in the dye solution to the TiO_2 surface. The distance between the dye skeleton and the point connected to the TiO_2 surface facilitates electron transfer from dye molecule to TiO_2. Hence, for a photosensitizer, the interaction and bond between the sensitizer (dye) and sensitizer (TiO_2) is vital in enhancing n of DSSC [17].

Photoaction spectra of the DSSCS provided further insights on the photoelectrochemical behavior of the family of natural dyes. The spectral response of lutein, chalcone and betanin pigment based DSSCs are shown in fig. 10. Normalized short-circuit current densities J_{sc} are plotted for different wavelengths of incident light.

Cosmos sulphureus showed the best photoelectrochemical behavior when compared to other flowers. Peaks were observed at wavelengths of about 505 nm and 590 nm, respectively verifying the charge injection from the excited state of the natural sensitizer. When light impinges on TiO_2, electrons in the valence/HOMO absorb photons with energy greater than or equal to TiO_2

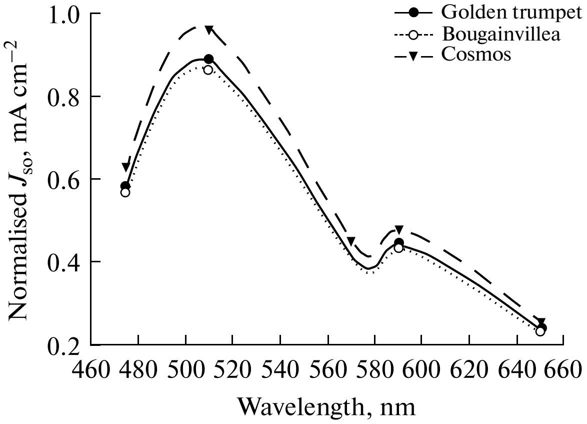

Fig. 10. Spectral response of golden trumpet, bougainvillea and cosmos sensitized DSSC.

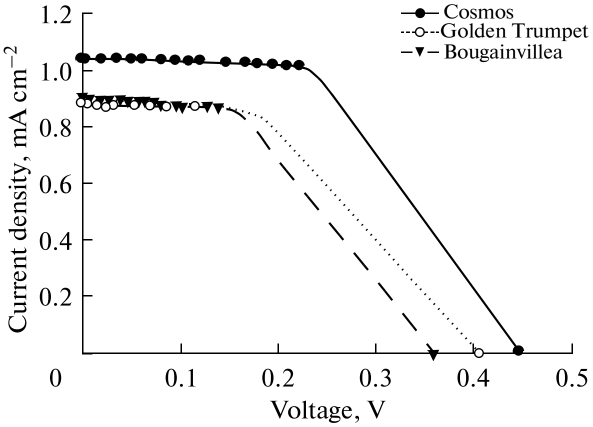

Fig. 11. I–V curve for cosmos, golden trumpet and bougainvillea sensitized DSSC.

bandgap. These electrons jump into the conduction/LUMO, leaving holes in the HOMO. Thus the absorption of a photon generates an electron/hole pair, called an exciton that can be exploited for charge transport [18].

The dye molecules absorb visible light and inject electrons from the excited state into the metal oxide conduction band. The injected electrons travel through the nanostructured film to the current collector and the dye is regenerated by the electron donor in the electrolyte solution [19]. This light-driven electrochemical process in DSSC is regenerative. I–V plots of the natural dye based DSSCs are shown in Fig. 11.

The efficiency of natural dye based DSSC is correlated to the maximum absorption coefficient of the dye and the interaction of the dye molecules to the TiO_2 surface. It is also dependent on intensity and range of the light absorption of the extract on TiO_2. Higher interaction between

TiO_2 and dye molecules leads to better charge transfer. The various photovoltaic parameters for DSSCs sensitized by golden trumpet, bougainvillea and cosmos flowers are shown in table.

Cosmos sulphureus showed the highest efficiency of 0.54% followed by *Allamanda cathartic* producing 0.40% efficiency and *Bougainvillea spectabilis* at 0.38%. Cosmos also produced the highest J_{sc} of 1.041 mA cm^{-2}. Open circuit (V_{oc}) values for all natural dye based DSSCs were quite promising with cosmos yielding the maximum value of 0.447 V, closely followed by golden trumpet and bougainvillea at 0.405 and 0.359 V respectively.

Photoelectrochemical parameters of natural-dye based DSSC

Photosensitizer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
Cosmos	0.447	1.041	0.61	0.54
Golden trumpet	0.405	0.878	0.54	0.40
Bougainvillea	0.359	0.898	0.52	0.38

CONCLUSIONS

DSSCs were fabricated using natural dyes such as golden trumpet, bougainvillea and cosmos. Constant current EPD method was employed to prepare TiO_2 films. The absorption and adsorption spectrum of the dye were analyzed using UV–VIS spectrophotometry. Interaction between TiO_2 and dye molecules leads to better charge transfer which affects the n of DSSC. *Cosmos sulphureus* showed the highest efficiency of 0.54% followed by *Allamanda cathartic* producing 0.40% efficiency and Bougainvillea spectabilis at 0.38%.

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