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Natural Dyes as a Photosensitizer in Dye Sensitized Solar Cells- Review

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Abstract: **Synthetic metalo-organic dye sensitized solar dyes show better efficiency but difficult to prepare in pure form and are not cost effective. Natural dyes based solar cells are more easily fabricated. Natural dyes or pigments can be obtained from fruits, seeds, leaves, roots, and flower. This review gives an insight into different types of natural dye photosensitizer containing Anthocyanins, Chlorophyll, Flavonoid, Xanthins and Carotenoids which can be co-sensitized to give better efficient Dye Sensitised Solar cell and has broad scope for research.**

Index words: Anthocyanins, Betacyanin, Dye sensitized solar cells, Natural dyes, Photosensitizer

I. INTRODUCTION

In recent years, due to the rapid depletion of fossil fuels there is a search for environmental amiable materials following the green chemistry route. Solar cell research has undergone a tremendous development from photovoltaic cell to Dye sensitized solar cell (DSSC). DSSC developed by Grâtzel and coworkers (1991) are a class of cost-effective and environmental friendly solar cells. Traditionally, the DSSC consist of transparent conducting oxide glass (TCO) (Fluorine-doped tin oxide or Indium-doped tin oxide), nano-crystalline semiconductor (TiO_2, ZnO, SnO_2) anode, dye as photosensitizer, Iodine electrolyte, and cathode as shown in Fig. 1 & Fig. 2 (Iftikhar et al, 2019). Constant efforts have been made to develop dye sensitized solar cells to improve its efficiency, durability and cost by modifying photo-electrode, electrolyte and photosensitizers. Recently, the utilization of natural pigments from plants as sensitizer for a DSSCs is under progress. It appears to be the best alternative compared with ruthenium (Ru) based DSSC in aspects of low cost, biocompatibility, easier preparation, and abundant availability.

II. NATURAL DYES

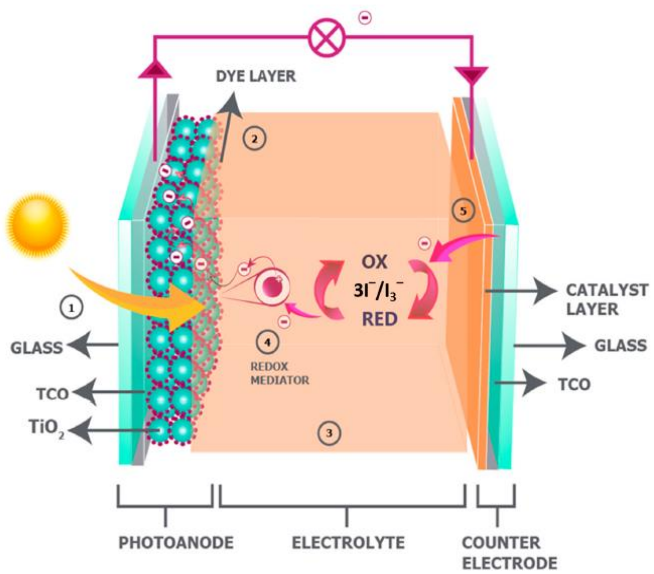

Fig. 1. Schematic representation of DSSC

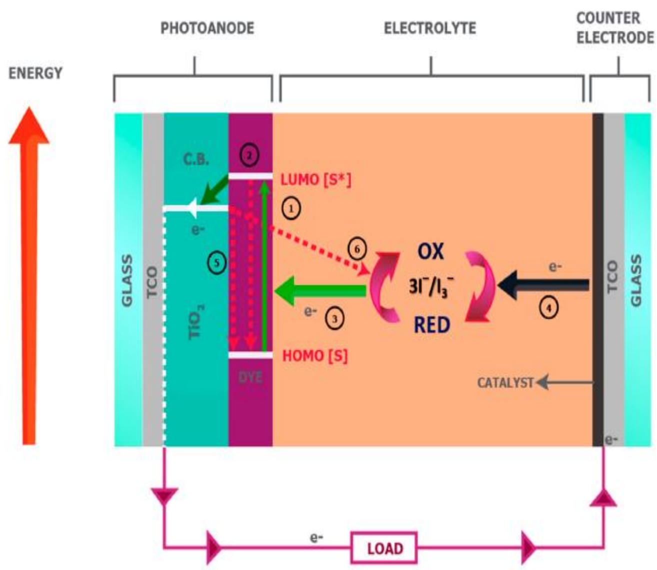

Fig. 2. Operating mechanism of DSSC

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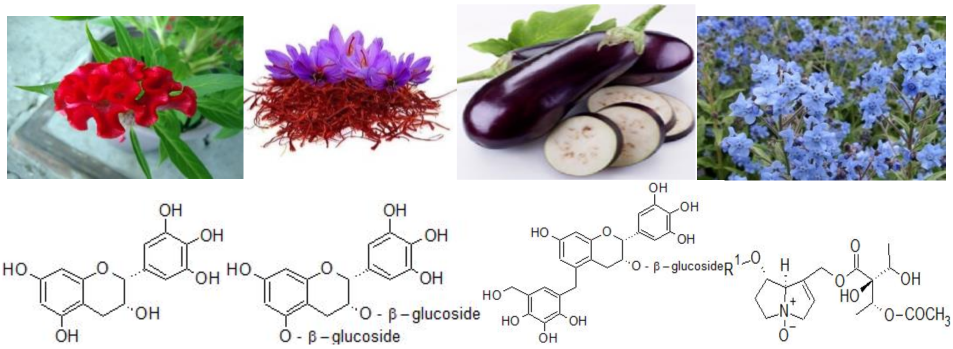

Fig. 3. a. Celosia Cristata b. Saffron c. Eggplant peel d. Cynoglossum

Anthocyanins are found in the flowers and fruits, these flavonoid pigments are used as photosensitizer in DSSC. The Carbonyl, carboxyl, and hydroxyl groups present in these anthocyanin molecules improve the adsorption ability of dye on TiO_2 and therefore facilitate easy charge transfer. It was found that the natural dyes show low efficiency due to instability and poor interaction as compared with synthetic dyes used as sensitizer in the DSSC. The efficiency of DSSC was found to improve by the forming two buffered layer with Algalinate and spirulina over the TiO_2 film before sensitizing with anthocyanin dye which is used as photoelectrode in DSSC (Prabavathy, et al, 2018). The influence of turmeric natural dye adsorption onto TiO2 based DSSC's photoanode has been studied by using XRD, UV-Vis- NIR spectroscopy, EDS and SEM to investigate structural properties, optical properties and surface morphology of dye free and dye adsorbed photoanodes. Light absorption and transmittance capacity changed dramatically in the dye adsorbed sample and optical band gap change confirmed the adsorption of the dye on the nanoporous surface revealing the enhanced effect of dye on the optical properties. (Khalid et al, 2018). Anthocyanins dyes extracted from Celosia Cristata, eggplant peel and Cynoglossum and flavonoids extracts from Saffron petals (fig. 3) could be fabricated on TiO_2 layer of DSSC due to presence of carbonyl and hydroxyl groups. The studies were done to evaluate electrochemical properties, photovoltaic properties and absorption spectra of these dyes for their efficiency as a photosensitizer for DSSC. The highest power conversion efficiency was ca. 1.38%, which belonged to Celosia Cristata extract (Hosseinnezhad et al, 2018). The natural sensitizers from avocado peel, blueberry and pomegranate were used in the fabrication of DSSC and the research result reveals that Avocado peel shows the highest efficiency due to lowest energy band gap compared to pomegranate and blueberry dyes (Hamid, Suhaimi, & Yatim, 2018). The natural dyes extracted from St. Lucie cherry, yellow jasmine, and madder berries were reported to act as a sensitizer in DSSCs. This was compared with bare TiO_2 photoanode, and natural dye–loaded photoanodes demonstrates far higher absorption ability in the visible region (Atli, et al, 2019). Efficiency of DSSCs can be enhanced by co-sensitization using natural pigments. The natural pigment betanin co-sensitized with indigo and lawsone pigments were investigated using density functional theory (DFT). The betanin/lawsone co-sensitized solar cell showed enhancement in efficiency due to efficient charge separation and charge transfer in lawsone as compared to indigo pigment (Sreeja & Pesala 2019). Extraction of natural dyes like Betalains from Bougainvillea Bracts & beetroots and anthocyanins from eggplant using different solvents and adsorption on TiO_2 photoanode was studied and compared the efficiency with the N719 DSSC (García-Salinas & Ariza 2019). Extracts from Cassia fistula (C. fistula) flower (fig. 4) were used as photosensitizer to fabricate titanium di-oxide (TiO_2) based DSSC. The studies were carried out using the

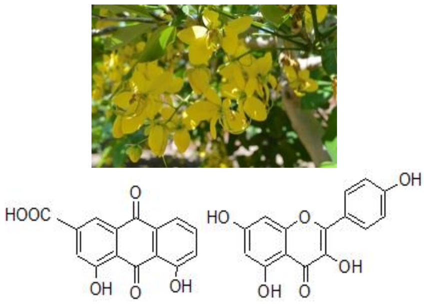

Fig. 4. Cassia Fistula: Rhein & Kempeferol

DFT to estimate the energy level (HOMO-LUMO) of dye component of C. fistula. The UV-Visible absorption spectra of dye solution and dye loaded on TiO2 photoanode showed broader absorption band in the visible range making the dye extracted from C. fistula flowers a promising photosensitizer (Chandra Maurya et al, 2019). Active pigments of carbazole alkaloids and anthocyanins were extracted from the fruits of Murraya Koenigii and flowers of Hibiscus Sabdarifa and mixture of these dyes were fabricated on to the DSSC's to study the performance. It was found that the energy gap was lower than the each individual dye by UV-Visible absorption spectra (Rajkumar et al, 2019). DSSC was fabricated with the mixtures of natural green (extracted from Malabar spinach) and red (extracted from red spinach) dye to improve the conversion efficiency of the cell. DSSC co-sensitized with the optimum combination of dyes (20% green+80% red) exhibited the highest cell efficiency of 0.847% under 100 mW/cm^2 illumination at AM 1.5G condition which was higher than the individual dye (Kabir, et al, 2019). Similar studies were done by Bashar et al, (2019) to extract the natural pigment betacyanin red dye (fig. 5) from beetroot (Beta vulgaris) and the pigment chlorophyll green dye from spinach (Spinacia oleracea) which was used as a sensitizer source for natural dye-based DSSC.

In the UV absorption spectrum, the combination of dyes showed a wide absorption spectra and higher absorbance in the visible solar spectrum than both the single individual red

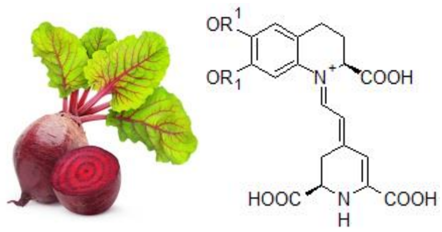

Fig. 5. Beetroot: Betacyanin

or green dye (Bashar et al, 2019). The methanol extracts of flowers of Canna lily Red (*Canna indica L*) and Canna lily yellow (*Canna indica Flava*) containing anthocyanins (fig. 6.) were studied extensively as a potential photosensitizers with TiO_2 as photoanode and concluded that the optimization was required to enhance the power conversion efficiency (Sahoo et al, 2020).

Malaysian fruit, betel nut (*Areca catechu*), was used to obtain a new natural dye to use as a sensitizer in DSSCs. This fruit contains tannins, polyphenols, gallic acid,

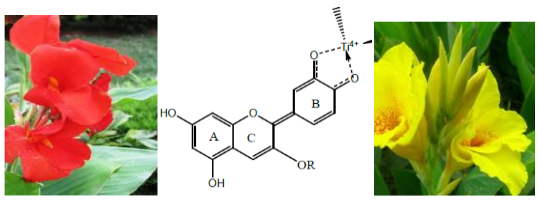

Fig. 6. Canna lily Red - Canna lily yellow

catechins, alkaloids, fat, gum, and other minerals. Gallotannic acid, a stable dye, is the main pigment (yellowish) of *A. catechu* and it is responsible for the effective absorption of visible wavelengths. The natural organic dye obtained from A. catechu was incorporated with the co-adsorbent chenodeoxycholic acid (CDCA) and assembled in to DSSC. The photo-electrochemical characteristics and photovoltaic efficiency of this dye was evaluated by fabricating a DSSC (Najm et al, 2020). Anthoxanthin based dyes extracted from Moringa flower and yellow rose also containing Kaempferol (K) and Quercetin (Q) were characterized and time dependent density functional theory (TD-DFT) was used to study the optical properties and compared with the experimental findings. The efficiency of natural dyes could be modified by introducing some anchoring groups into these dyes (Megala, Mayandi, & Rajkumar, 2020). Based on the previous studies Carvalho et al, (2020) research group used 2, 2'- bipyridine (bipy) as electrolyte additive in the DSSCs prepared using carotenoid pigments extracted from Annatto (Bixa orellana) fruit seeds which are rich in red pigment Bixin (Bx) and Norbixin (NBx) molecules. The study based on photoelectrochemical properties and potential voltage (PV) output and current density revealed that bipy additive in the electrolyte of DSSC sensitised with Bx and NBx showed increase in the voltage and current density of the solar cell. Number of research studies has shown that combination of two different natural dyes as a photosensitizer shows photostability and synergistic effect in the photovoltaic performance of DSSC. The pigment betalin extracted from New Mexico prickly pear (Opuntia phaeacantha) and anthocyanin from New Mexico mulberry (Morus rubra) was used as sensitizer in Solar cells prepared using nano-crystalline TiO_2 mesoporous films. The DSSC fabricated with these natural dyes, betalain extracts from prickly pear yielded higher PV output and efficiency, while anthocyanin pigment extracts from mulberry gave better photo-stability (Obi, Frolova, & Fuierer, 2020). The potential of dye extraction from four native plants Crocus sativus (Saffron), Allium cepa L (red onion), Malva Sylvestris (Mallow), and Oregano (Origanum vulgare) (fig. 7.) was evaluated by fabricating DSSC and characterization by absorption spectra as well as electrochemical and photochemical properties.

These dyes were considered as excellent light harvesting pigments and effective for charge generation from sunlight. The photoelectric conversion efficiency of these natural dyes were found to be less than 2% as observed in many

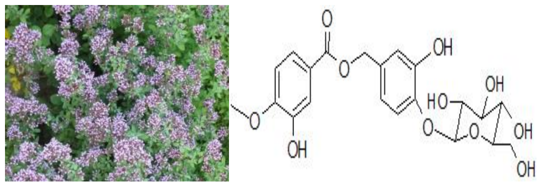

Fig. 7. Oregano (Origanum vulgare)

different natural dyes mentioned in the literature (Jalali et al, 2020). The behaviour of DSSCs with double layer photoanodes using graphene oxide-titanium dioxide (GO-TiO2) and TiO2 layers analysed with chlorophyll based plant dye as photosensitizer extracted from highly sensitive Mimosa pudica while studying the effect of varying GO content. It was also compared with to that of single-layer pristine TiO2 photoanodes sensitized with chlorophyll and anthocyanin dyes i.e. Hibiscus rosa-sinensis and Rhoeo spathacea. The enhanced performance of the DSSCs was attributed to the incorporation of the nanocomposite layer using GO and also it was found that Hibiscus rosa-sinensis showed remarkable efficiency in the DSSC as a photosensitizer compared with other two dyes (Mensah-Darkwa et al, 2021). Natural dye extract from pomegranate and N719 dye based DSSC were fabricated for a comparative studies using UV-Visible spectroscopy, photovoltaic characterization and impedance spectroscopy to optimize various components for developing cost effective commercially available natural DSSC (Faraz et al, 2021). To enhance the photosenistizer efficiency and stability of the anthocyanin dye obtained form rose petal, it was co-sensitized with Astaxanthins extracted from *Haematococcus Pluvialis*, which encircles the anthocyanin and scavenges the free radical produced due to photocatalytic activity (PCA) and reduces the photodegradation (Prabavathy, et al, 2021).

CONCLUSION

Natural dyes and pigments showed promising properties as light harvesting sensitizers. The suitable LUMO energy level, as well as the lower band-gap, of the extracted pigments, illustrated them as the efficient sensitizer for utilizing in fabricated DSSCs. Co-sensitizer also improves the phtocatalytic activity and reduce the photodegradation of these dyes. Due to the existence of carbonyl and hydroxyl groups, it enables them to bind to the TiO_2 layer, as a result, improve the electron migration, as well as, enhance the energy conversion efficiency of the fabricated DSSC. As a result, due to the low-cost, eco-friendly, and technical efficacy of the extracted pigments, natural dyes have good scope for the development of DSSCs production on an industrial scale if the photoelectric conversion efficiency can be matched with that of Ruthenium based DSSC.

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