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A Review- The Potential of Natural Dyes for Dye Sensitized Solar Cells

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Abstract:-Technologies are developing day by day. The main threat to the environment is the generation of greenhouse gases due to the combustion of fossil fuels [2]. It affects the survival of living organisms. Renewable energy is essential for the society [3]. The most demanding renewable source, solar energy is replaced instead of fossil fuel. Solar energy is the inexhaustible source of energy on earth [4]. Dye sensitized solar cells (DSSC) is working based on the solar energy. The present research is to produce a highly efficient DSSC. In this review paper, we are dealing with natural dyes, various pigments in the dye and sort out the potential of various natural dyes from various research articles.

Keywords: - Renewable Energy, Solar Energy, DSSC, Natural Dyes.

I. INTRODUCTION

In growing world, the technologies are getting advanced. As modernization and industrial growth is increasing day by day the use of energy is also increasing. Greenhouse gases such as carbon dioxide, methane etc. are obtained due to the combustion of fossil fuels, this may leads to the pollution, global warming and also climatic changes [2,5]. Fossil fuels are depleting rapidly due to this, alternative energy source are required [3].Hence, to avoid this situation researches are going on to replace fossil fuel by solar energy [2].

Solar energy is the radiant heat and light coming from sun. It is the inexhaustible source of energy on earth. Solar cells are the devices which are used to convert solar energy into electrical energy. These cells works on the principle of photovoltaic effect. They are made up of semiconducting material, which is having a property of absorbing light. Solar cells can be classified into first (conventional or traditional), second (thin film) and third generation cells. The conventional crystalline silicon cells and thin film cells are less efficient, high cost and the stability of the absorber materials is less [3]. The researchers are going on in order to achieve low cost and highly efficient solar cells. Third generation solar cells are described as emerging photovoltaics. Dye sensitized solar cells (DSSC) are third generation solar cells [8], invented by Brian O' Regal and Michael Gratzel in 1991 at Switzerland [3,5, 6]. This technology is developing fastly due to its light weight, flexible nature, non-polluting nature, low cost, eco-friendly, easy to manufacture, attractive appearance and high conversion efficiency [5].

II. WORKING PRINCIPLE OF DSSC

DSSC is a device used to convert solar energy into electrical energy based on photosensitizer with wide band gap semiconductor [2]. It is constructed by sandwiching two fluorine doped indium tin oxide (FTO) glass plates by some electrolytes [3]. Light source, semiconductor, photosensitizers, electrolytes and counter electrode play a vital role in the construction of DSSC [4, 6]. Each layer of the cell has their own activities. FTO glass plates are transparent in order to light source to pass through. To increase the electrical conductivity and light transmittance the FTO glass plates are using.

Semiconductor is a compound that can conduct the electrons. Semiconductor used for DSSC should possess wide band gap [5]. The materials such as TiO_2, ZnO, Nb_2O_5, SnO_2 and CdO which are having band gap of 3.2eV,3.2eV, 3.4eV, 3.6eV and 2.5eV [24] respectively are used as semiconductors in DSSC. Evenif the band gap of TiO_2 and ZnO is same but energy level of ZnO is less than TiO_2. TiO_2 is preferred mostly, due to its low cost, non-toxic nature, chemical stability and having high refractive index [2,4,7].TiO_2 can absorb both UV and visible light by the help of suitable photosensitizers.

Photosensitizer plays a vital role to determine overall efficiency of the cell [4,5]. Synthetic and natural dyes are used as photosensitizers. Ruthenium based synthetic dyes are more efficient dye for photo sensation. Natural dyes are preferable because synthetic dye have harmful effects such as allergic, carcinogenic etc. Electrolyte commonly used in DSSC is tri iodide/ iodide (I_3^-/I^-) electrolyte [4,6]. Electrolyte influences theconversion efficiency of DSSC. It has high chemical and thermal stability, non-volatility, and electric conductivity [20]. Last but not the least, the counter electrode should possess

high photo conversion efficiency and catalyze the redox reaction with electrolyte [6]. Platinum or carbon is mainly used as counter electrode [4]. Reduction of the mediator takes place in counter electrode. Counter electrode is made by coating platinum or carbon electron in FTO glass [20]. It enables electron transfer from external circuit to the electrolyte.

Semiconductor layer is coated on the conducting side of the FTO glass and loaded with a layer of dye [7]. This coated glass and counter electrode are sandwiched using an electrolyte and further measurements are carried out [3, 4]. The sunlight falls on the semiconductor glass side. Due to the presence of photosensitizer the molecule getsphoto excited and quickly inject electron into conduction band of the semiconductor into an outer electrical circuit to generate electric current [6]. Electrolyte reacts with photosensitized absorber. It will affect the open circuit voltage by decreasing the concentration of electron in the conduction band. The electricity is conducting through counter electrode.

III. PHOTOSENSITIZERS

Photosensitizer is a molecule which makes chemical change in another molecule in a photochemical process. It plays a vital role to increase the overall efficiency of DSSC.

Requirements of photosensitizer [4, 5,8]

- Strong absorption
- Efficient to convert solar energy into electricity
- Capable of injecting electron into semiconductor layer upon excitation.
- Carry suitable anchoring groups (-COOH,-OH) to bind itself with semiconductor layer.
- Ability to resist oxidation and reduction without any degradation.

India has rich biodiversity with natural products, one such product is dye. Dyes act as a photosensitizer and begin to generate power. It actsas an absorber of sun's radiation. Dyes don't possess any harmful effects to environment. Dyes can be classified as organic dye and inorganic dye [8]. Organic dyes and inorganic dyes are also known as natural dyes and synthetic dyes respectively.

IV. NATURAL DYE

Natural dyes are used in DSSC instead of expensive synthetic dyes because of their low cost, eco-friendly, and non-toxic nature. Natural dyes are mainly occurring from plants. Natural dye can extract by simple procedure.Every part of the plants can use as natural dye [8]. Natural dye contains plant pigment such as Flavanoids, Chlorophyll, Carotenoids, Tannins and Betalains. Table: 1 shows various pigments in plants [4].

Pigment	Category	Present In
Flavanoids	Anthocyanins	Bryophytes Gymnosperms Angiosperms Ferns
	Flavanols	
	Chalcones	
	Proanthocyanidins	
	Aurones	
Chlorophyll	Chlorophyll a	All photosynthetic plants Cyanobacteria Algae
	Chlorophyll b	
Carotenoids	Carotenes	Crustaceans Bacteria Photosynthetic plants
	Xanthophyll	
Tannins	Hydrolysable tannins	Gymnosperms Angiosperms
	Condensed tannins	
Betalains	Betacyanins	Caryophyllates Fungi
	Betaxanthins	

Table 1: Various Pigments in Plants

V. FLAVONOIDS

Flavonoids are biological pigments, which are present in bryophytes, gymnosperms, angiosperms and ferns. It has a structure based on 15 carbons with 2 phenyl rings are connected by 3 carbon bonds (C_6-C_3-C_6) [25]. It has the ability to absorb visible light. According to the nomenclature of the flavonoids it can be classified into bioflavonoids, isoflavanoids and neoflavanoids. Depend upon their structure it can be categorized as anthocyanins, flavanols, chalcones, proanthocyanidins and aurones [8].

Flavanoids plays a vital role in colouring of plants. Due to this colour it will attract pollinators such as bees, birds etc. Leaves which contain this pigment, helps to protect plant by screening out harmful gases from sun. Anthocyanin is the mainly group among flavonoids [4]. Flavonoids can be seen in blueberries, black tea, citrus, cocoa, mulberry etc.It is responsible for the absorption of light is visible region [25] due to its larger wavelength and colour. Kenaf hibiscus has flavonoid pigment, which is highly efficienti.e. 2.87% efficiency [9].

VI. CHLOROPHYLL

Chlorophyll is the green coloured biological plant pigment which is present in all photosynthetic plants, cyanobacteria and algae [25].There is two types of chlorophylls, chlorophyll a and chlorophyll b [5]. Chlorophyll is a chelate compound, which is composed of carbon, hydrogen, oxygen, nitrogen and magnesium ions. Chlorophyll a and Chlorophyll b has a nomenclature of $C_{55}H_{72}O_5N_4Mg$ and $C_{55}H_{70}O_6N_4Mg$ respectively [25]. Chlorophyll has an important role in absorption of light due to the presence of magnesium ions [5].

Chlorophyll plays a vital role in the photosynthesis of plants [5], thereby convert carbon dioxide into carbohydrates and water into oxygen.Spinach has chlorophyll pigment, which is 1.131% efficient [14].

VII. CAROTENOIDS

Carotenoid is biological plant pigment which is present in photosynthetic plants, crustaceans and bacteria [25]. Carotenoid is also known as tetraterpenoids [8].It has the structure of polyene hydrocarbon with and without oxygen which is known as carotenes and xanthophyll respectively [3,8].Lutein and zeaxanthin are the types of xanthophyll, similarly α-carotene,β-carotene and lycopene are different types of carotenes [25].

Carotenoids plays important role in absorbing light for photosynthesis and also act as aprotecting shield for chlorophyll in plants [25]. It also helps in the metabolism of the plants. These pigments are usually in red, orange or yellow pigments [8]. Ivyground has carotenoid pigment with 0.24% efficiency [12]

VIII. TANNINS

Tannins are biological plant pigments, which are present in gymnosperms and angiosperms. Depend on nomenclature tannin can be classified as hydrolysable tannins and non-hydrolysable tannins or condensed tannins. Tannins are severe, bitter plant polyphenols that shrinks proteins. Tannins are found in leaf, bud, seed, root and stem of the plants [22].

Tannins are secondary metabolites, which are phenolic in nature [22]. Tannins don't restrict the metabolism in plant but restricts the digestive processes. . Tea plant is having high content tannins. Mimosa, quebracho, chestnut, valoneaetc. Are examples of tannin pigment [22, 23].

IX. BETALAINS

Betalains are biological plant pigments, which are present in fungi and caryophyllates [4]. They are mainly found in petals of flower in plants. It can be seen in red to purple colour. Depends on the colour pigments betalains can be classified as betacyanins and betaxanthins [4]. Betanin, isobetanin, probetanin and neobetanin, which has red to violet betalain pigments. Similarly, vulgaxanthin, miraxanthin, portulaxanthin and indicaxanthin [17], which has appear in yellow to orange betalain pigment.

Betalains has antioxidant property and light absorbing property. Betalains are stable in acidic environment [25]. This pigment has high potential. It has carboxyl group inorder to stick with the semiconductor layer. Red and violet bougainvillea glabra contains betalains pigment, which are 0.45% and 0.31% efficient. [17]

Sl No.	Natural dye	Efficiency(ɳ)	Reference
1	Kenaf Hibiscus	2.87	9
2	Mangos teen pericarp	1.17	10
3	Purple Cabbage	0.75	11
4	Wormwood	0.538	11
5	Ivy ground	0.08	12
6	Red frangipani flowers	0.3	12
7	Rosella	0.37	13
8	Blue pea	0.05	13
9	Spinach	1.131	14
10	Ipomoea	0.278	14
11	Nerium Oleander	0.061	15
12	Pink Bougainvillea	0.053	15
13	Red Hibiscus	0.19	15
14	Red bougainvillea glabra	0.45	16
15	Violet bougainvillea glabra	0.31	16
16	Red Bougainvillea spectabilis	0.48	16
17	Violet Bougainvillea spectabilis	0.35	16
18	Flame tree flower	0.2	17
19	Pawpaw	0.2	17
20	Dragon Fruit	0.22	18

Table 2: Potential of Various Natural Dyes

X. SYNTHETIC DYE

Synthetic dyes are also known as inorganic dyes. Photo degradation is more for synthetic dyes. Synthetic dyes used for photosensitizers are ruthenium (Ru) dye, osmium dye, iridium dye, unsymmetrical squarine dye, triphenyl amine etc. More efficient synthetic dye is ruthenium dye. Ru is highly efficient dye, which is having conversion efficiency of 11% [5]. Osmium dyes are 50% less efficient than Ru dye. Iridium has an overall conversion efficiency of 2.16% [7]. Unsymmetrical squarine dye [4] and porphyrin dye [5] an efficiency of 6.74% and 12% respectively. Synthetic dyes are costly, take time consuming procedures and are not easily extractable. So that synthetic dyes are trying to replace by natural dye [4].

XI. CONCLUSION

Lots of study and research works are going on DSSC. In this review paper, we discussed about natural dyes, various plant pigments present in natural dye and potential of some of the natural dye from various research papers. DSSC prefers natural dye due to its eco-friendly nature, non-toxic, easy availability and low cost [8]. Since the DSSC using natural dye has low efficiency, so can't go for larger production. The natural dye extract contains oils, alkaloids, steroids, saponins etc. other than plant pigment. This may affect the efficiency of the cell, so viable method is required for the purification of the natural dye. The highest efficient natural dye is 2.87%, which is extracted from kenaf hibiscus. The results of potential of the natural dyes are hopeful.Researches are going on inorder to develop the area of sensitizers for DSSC.

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