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ABSTRACT

Renewable energy sources are becoming imperative due to the high population, high demand energy and depletion of fossil fuels. The solar cells play important role in this regard. The third generation of solar cell has semiconductor electrode, dye, electrolyte, surfactant and counter electrode components. Among all of the components, dyes and surfactant perform a primary role in absorbing solar energy and converting it to electrical energy and storage capacity. The efficiency of working cells absolutely depends on the type of substance used as dye and surfactant.

Keywords: Energy, Solar Cell, Dye sensitizer, Natural dye, Surfactant.

1. INTRODUCTION

Due to the high demand of energy, reduction of fossil fuels and limitation of non-renewable energy sources [1], renewable energy sources becoming more important in the current scenario. Energy is a main resource for the progress of human civilizations and day by day demand is increasing constantly [2]. However, the existing plan of delivery and use of energy is untenable and it should be stabilized in the short time perspective. Electricity can be obtained from numerous sources such as biomass, coal and natural gas [3] and these fossil fuels burning have a disaster impact on the environment. Perpetuation of environment, during the energy manufacturing is Consequently, decisive. the energy production techniques should be reoriented towards renewable sources [2]. Solar photovoltaic technology has wonderful immense potential energy contribution [4] which can accomplish the energy demands of the world and this technique use to conversion of sunlight into electricity energy [5].

Three categories of photovoltaic solar cells are investigated till now by scientists [6]. The first category which is known as first generation is based on crystalline silicon material [7, 8]. The second category which is called thin-film technology is mostly based on CdTe, CdS, amorphous silicon (a-Si) and CIS/CIGS. The third type of solar cells is dye-sensitized solar cells (DSSC) [6-8]. DSSC is cost effective cell, due to low-cost materials and effortless fabrication process [7, 8]. DSSC consists of semiconductor electrode, dye, electrolyte, surfactant and counter electrode. Among all of the components, dyes and surfactant perform a most important role in absorbing solar energy and converting it to electrical energy and storage capacity. Therefore, the DSSC performance absolutely depends on the type of dye sensitizer and surfactant used [9, 10]. This review aims to symbolize recent studies of dyes and surfactant that have provided vital pathways towards superior device performance.

2. DYE SENSITIZER

Different dye sensitizers in order to achieve as an excellent dye sensitizer are:

2.1. Ruthenium (Ru) complex photosensitizers

Ruthenium based DSSC are characterized by excellent chemical stability with absorption of solar radiation in a wide range resultant it showed high efficiency. Scientists developed a lot of sensitizers based on ruthenium metal. Among them, the mainly recognized and extensively used are N3 (red dye), N749 (black dye), N719 and Z907 complexes [11, 12]. The N3 (red dye), and N749 (black dye) dyes are frequently used as indicator ones. However, all of ruthenium based DSSC obtain similar efficiency on the level of 10-11% [11, 12]. Ruthenium complexes have a strong tendency to degrade in the water environment [13] and create harmful impact on the environment by their chemical nature so in the last few years, stagnation was observed in ruthenium based assemblies [13].



Fig. 1: N3 Dye



Fig. 2: N719 Dye

2.2. Metal-free organic dyes

Due to high molar absorption, broad diversity of molecular structures with flexibility for molecular designing and low cost organic dyes are used in dyesensitized solar cells [14]. However, in comparison to metal complexes-based dyes, they obtained lower conversion efficiencies. The key factor which can limit the effectiveness of working DSSC sensitized with metal free organic dyes are the occurrence of dye aggregates formation on the surface of TiO₂ nanoparticles which caused suppression of the excited state of the sensitizer molecules Alizarin, coumarin, [14]. cyanine, triphenylamine, carbazole etc. based sensitizers which obtained the efficiency up to 5-9% [15], can be underlined. Alizarin, one of the metal free organic dyes has broad absorption (400-600 nm) with the strongest peak at 432.5 nm [16]. This dye is characterized by fast

injection electrons into the semiconductor conduction band with the indirect mechanism.



Fig. 3: Alizarin

Tsao et al. [17] observed the power conversion competence of 10.3% by exercise of two metal free organic sensitizer's i.e. organic dye (Y123) with cobalt base electrolyte. Kakiage et al. [18] reported that sensitized DSSC with ADEKA-1 and a carboxy-anchor organic dye of LEG4 collaboratively show an outstanding efficiency up to 14.30%.

2.2.1. Chlorophyll

Since chlorophyll is present in almost all plants so it is one of the plentiful dye and is extracted from leaves [19]. This dye can absorb the light from red, blue and violet wavelengths [19]. This pigment reveals absorption peaks between 430-662 nm range [19] and is used as dye sensitizer in DSSC [19].



Fig. 4: Chlorophyll

Chlorophyll pigment from three different plants (figs, apricot and cream) leaves gave different performances for DSSC [20]. The maximum absorption peaks were

attained at 413 nm, 394 nm and 415 nm for figs, apricot and cream leaves respectively. Chlorophyll pigments extracted from figs leaves demonstrated electrical performance of Jsc=2.09 mA/cm², Voc=0.60 V, FF=0.52 and energy conversion efficiency of 0.64% [20]. While chlorophyll pigments from apricot leaves showed electrical performance of Jsc=0.52 mA/cm², Voc=0.62 V, FF=0.55 and energy conversion efficiency of 0.26% which is lower than that observed for figs leaves [20]. The electrical performance for the DSSC with cream leaves dye illustrated the Jsc=2.28 mA/cm², Voc=0.61 V, FF=0.44 and energy conversion efficiency of 0.64% [20]. Dye extracted from olive, Lyceum shawii and Zizyphus leaves have also been tested as dye sensitizer in DSSC [21]. Zizyphus leaves showed electrical performance with $Jsc=1.50 \text{ mA/cm}^2$, Voc=0.68 V, FF =0.40 and energy conversion efficiency of 0.40% and for this reason the best dye sensitizer among the three leaves. It showed the highest absorption peak at 432 nm and 664 nm that signifying it to be chlorophyll group.

To give an eco-friendly device, chlorophyll dye extracted from *Azadirachta indica* leaves illustrated the electrical performance of Jsc= 0.43 mA/cm^2 , Voc=0.40 V, FF=0.40 and energy conversion efficiency of 0.72%which is considerably high for chlorophyll group dye sensitizer [22]. *Azadirachta indica* leaves have the maximum absorption peaks at 471 nm and 662 nm.

Chlorophyll pigment extracted from *Pandanus amaryllifolius* has highest absorption peaks at 415 nm and 661 nm [23]. This dye exhibit the electrical performance of Jsc=0.40 mA/cm², Voc=0.55 V and FF=0.61 that permits it to convert 0.10% of photon into electrical energy. Among all chlorophyll pigments as dye sensitizer in DSSC, the performance of dye extracted from *Azadirachta indica* leaves is best with the energy conversion efficiency of 0.72%.

Taya et al. [24] examined the chlorophyll extraction from *anethum graveolens*, parsley, arugula, *spinacia oleracea*, and green algae. Fresh or dried leaves from above mentioned plants influence strongly the adsorption of chlorophyll onto the photoanode surface and accordingly the performance. Results were obtained for both pre and post drying and the best efficiency was observed for DSSC assembly sensitized by the *spinach oleracea* with drying process employed equals 0.29%. Kabir et al. [25] examined the stability of natural green dye extracted from spinach leaves (*Spinacia oleracea*), prepared with methanol and found assemblies with an effectiveness of 0.398%. Wang et al. [26] have worked on chlorophyll dyes extracted from brown seaweed, *U. pinnatifida and*

examined two different types of chlorophyll and their oxidized forms. For each type of chlorophyll, they attained very high conversion efficiencies up to 3.40% and 4.60% for basic dyes; 2.60% and 2.50% for their oxidized forms.

2.2.2. Anthocyanin

Anthocyanin is a natural pigment in the plants which exhibited in purple-red color and absorb light within 450-600 nm range [27]. The presence of carbonyl and hydroxyl group in anthocyanin pigment allows to be attached with TiO_2 nanostructures that are significant parameters in analysis of the energy conversion efficiency of the DSSC [27]. When the dye molecules connect efficiently to the semiconductor materials nanostructure, more photon can be absorbed and converted in electrical energy [27].



Fig. 5: Basic Template Structure of Anthocyanin

Anthocyanin dye from Acanthus sennii Chiovenda flower extracted by Andargie and Ayele [28] have measured energy conversion efficiency which was 0.15% at 524 nm highest absorption peak with the $Jsc=0.49 \text{ mA/cm}^2$, Voc=0.57 V, FF=0.60. Energy conversion efficiency was recorded at 1.13% [29] with the highest absorption peak at 543 nm with Jsc=6.52 mA/cm², Voc=0.32 V, FF=0.55 by using of anthocyanin dye extracted from blackberry besides, red silician orange extract also used as natural dye sensitizer in DSSC [29] and this dye demonstrated highest absorption peak at 538 nm that resulting it to achieve 1.01% of energy conversion efficiency attributed by high Jsc=5.13 mA/cm², Voc=0.33 V, FF=0.59. Anthocyanin pigment from eggplant recorded the energy conversion efficiency of 0.64% attributed by Jsc=3.48 mA/cm², Voc=0.35 V, FF=0.53 and maximum absorption at 545 nm [29].

Ghann et al. have work on anthocyanin dye from Pomegranate and found highest absorption peak at 510 nm with high energy conversion efficiency of 2.00% amid Jsc=12.2 mA/cm², Voc=0.39 V, FF=0.41 [30]. Dragon fruit dye showed the highest absorption peak at 535 nm in DSSC and recorded high energy conversion efficiency of 0.22% [31]. Luffa cylindrica [27], poinsettia bracts [27, 32] black grapes [27], Saraca asoca flowers [27] and hibiscus [27, 33] also had been extracted to be used as the dye sensitizer in DSSC and recorded low energy conversion efficiency of 0.13%, 0.11%, 0.43%, 0.09% and 0.56% respectively. Calogero et al. [34] used aubergine, red Sicilian orange and blackberries in dyesensitized solar cells and found the efficiency of 0.64%, 1.01%, and 1.15%, respectively. The achieved DSSC worked on the Isc, Voc and FF parameters and data were 7.68 mA/cm², 348 mV and 0.43 respectively. Overall conclusion for anthocyanin dyes, the best extracted dye was pomegranate dye.

2.2.3. Betalain

Betalain pigments are also one of the most dye sensitizer in DSSC [27]. Betalain have carboxylic (-COOH) functional group that helps it to bind with TiO_2 . This pigment showed strong absorption between 400-600 nm [27].



Fig. 6: Basic Template Structure of Betalain

Betalain pigment extracted from purple wild sicilian showed high energy conversion efficiency of 2.06% with the Jsc=8.80 mA/cm², Voc=0.39 V and FF=0.60 [35]. This dye showed the highest absorption peak at 450 nm. Betalain pigment from *Bougainvillea glabra* flower [36] showed wide absorption peak in 480-650 nm range and related DSSC have recorded electrical performance of Jsc=3.72 mA/cm², Voc=0.44 V, FF=0.59 and energy conversion efficiency of 0.98% [27]. Betalain pigment from beetroot dye revealed the maximum absorption peak at 540 nm with the electrical performance of Jsc=2.32 mA/cm², Voc=0.66 V, FF=0.20 and energy conversion efficiency of 0.30%. Betalain dye extract from *Opuntia dillenii* exhibit electrical performance of Jsc=1.09 mA/cm², Voc=0.52 V, FF=0.69 and energy conversion efficiency of 0.47% [37.] Similarly, betalain dye from red turnip plant showed the highest absorption peaks at 480 nm and 549 nm [37] in DSSC and electrical performance achieved with Jsc=9.50 mA/cm², Voc=0.45 V, FF=0.37 and energy conversion efficiency of 1.7%. Overall, the best betalain pigments extracted from purple wild sicilian showed the highest energy conversion efficiency of 2.06%.

2.2.4. Flavonoid

Flavonoids have been extracted from various plants [38] and divided according to their chemical structure as follows: flavonols, flavones, flavanones, isoflavones, catechins, anthocyanin, and chalcones. All flavonoids do not have the ability to absorb visible light, although they have similar structures [38].



Fig. 7: Basic Template Structure of Flavonoid

The adsorption of flavonoid to the mesoporous TiO_2 surface is fast, displacing an -OH counter ion from the Ti sites that combines with a proton donated by the flavonoid structure [38]. The flavonoid dye extracted from *Jathopha curcas* can be used as a DSSC sensitizer and related solar cell is sensitized to achieve upto Jsc 0.69mAcm², Voc 0.054V, and FF 0.87, with a cell conversion efficiency of 0.12% [39].

2.2.5. Carotenoid

Carotenoid is a natural organic pigment and is usually responsible for yellow to orange petal colors [38]. Carotenoids are compounds which consist of 08 isoprenoid units and have huge potential as energy harvesters and sensitizers for DSSCs. Hemalatha et al. have worked on carotenoid dye isolated from *Kerria japonica* and reported that the conversion efficiency was 0.22% [40]. Yamazaki et al. studied carotenoids, crocetin and crocin dyes in DSSC. The translation competence of crocetin sensitized DSSCs (0.56%) is three times, or higher than crocin (0.16%), because of the presence of carboxylic groups in the crocetin compound [41].

Plant Name	Pigment/ Used Part of plant	λ _{max} (nm)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	Ref.
Acanthus sennii Chiovenda	Anthocyanin/Flower	524	0.49	0.51	0.60	0.15	[27]
Blackberry	Anthocyanin	543	6.52	0.32	0.55	1.13	[27]
Luffa cylindrica	Anthocyanin	430	0.44	0.52	0.60	0.13	[27]
Hibiscus	Anthocyanin/Flower	516	0.96	0.27	0.43	0.11	[27]
Saraca asoca	Anthocyanin/Flower	450	0.29	0.29	0.52	0.09	[27]
Apricot	Chlorophyll/Leaves	394	0.56	0.62	0.55	0.26	[27]
Olive	Chlorophyll/Leaves	432	0.85	0.59	0.33	0.17	[27]
Lycium shawii	Chlorophyll/Leaves	423	1.20	0.62	0.43	0.32	[27]
Zizyphus	Chlorophyll/Leaves	416	1.50	0.68	0.40	0.40	[27]
Pandanus amaryllifolius	Chlorophyll/Leaves	415	0.40	0.55	0.61	0.10	[27]
Bougainvillea glabra	Betalain/ Flower	535	3.72	0.44	0.59	0.98	[27]
Opuntia dillenii	Betalain	525	1.09	0.521	0.69	0.47	[27]
Red turnip	Betalain	540	9.50	0.45	0.37	1.70	[27]
Fructus lycii	Flower	425	0.53	0.68	46.6	0.17	[38]
Grapes	Flower	560	0.09	0.34	61.1	0.38	[38]
Hylocereus polyrhizus	Flower	535	0.20	0.22	0.30	0.22	[38]
Bixa arellana	Seeds	474	1.10	0.57	0.59	0.37	[38]
Green algae	Whole part	666	0.13	0.41	21.0	0.01	[38]

 Table 1: DSSC Performances based on Natural Dyes

Absorption wave length (λ_{max}), Short circuit current (J_{sx}), Open circuit voltage (V_{ax}), Fill Factor (FF), and energy conversion efficiency (η)

3. SURFACTANTS

Surfactants are used in photochemical process [42]. Surfactant molecules intermingle with dye by charge transfer or coulombic interaction and this interaction depending on nature of dye and surfactants [43]. Due to this character, it is used in DSSC. Zhi-Chu Bi *et al.* [44] has used sodium lauryl sulphate (SLS) as a surfactant in thionine dye and Fe^{+2}/Fe^{+3} as reductant and noted that SLS surfactant solution is used in cells to solublise the thionine in water [45]. Similarly, Srivastva et al. [46] has used polyvinyl methyl ether surfactant to improve conversion efficiency of the cells. Valenty [47] has worked on surfactants monolayer film and reported that methylene blue adsorption to photogalvanic electrodes is related to the orientation and absorption spectra of it's surfactant analogs in monolayer films.

SLS is extensively used as surfactant in the photogalvanic cells [48-50] but other surfactants are also used like Triton-X 100 (2-[4-(2,4,4-trimethylpentan-2-yl) phenoxy]ethanol) [51], Brij-35 [52], Tergitol-7 [53], CPC (1-cetylpyridinum chloride) [54], DSSS (dioctyl sodium sulfosuccinate) [55], CTAB (cetyltrimethylammonium bromide) [56] etc. for enhancement of electrical output of cells. Lal and Gangotri [56] have used mixed surfactants in the system of photogalvanic cell with better electrical output. It was revealed by scientists that the conversion competence of the systems with different surfactant is found to be in the order

anionic > nonionic > cationic, if dye is cationic [57]. In the opposite charge dye and surfactant, a stable dye surfactant complex is formed in which dye molecule is surrounded by surfactant micelles in some regular geometry which retards the intermolecular twisting results in an enhancement of fluorescence [58].



Fig. 8: Triton-X 100



Fig. 9: Brij-35



Fig. 10: Tergitol-7













4. CONCLUSION

The results of this study have given a number of ideas to fabricate a cell. The DSSC offers renewable way of use and electrodes with solution are non-consumables. Cells, which are source of energy, shall be cost effective and eco-friendly. In brief, this review awares about low cost production, environmental friendly, inherent storage capacity and wide availability of components of cell.

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Conflict of Interest

Nil

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