CHAPTER-2

LITERATURE SURVEY

2.1 Introduction

The operational principle of DSSC

A dye-sensitized solar cell (DSSC) is mainly different from other solar cells due to its structure. It consists of a TCO plate, a photoanode (nano-sized semiconductor coated on), a dye attached to the semiconductor, a redox mediator (electrolyte), and a counter electrode [25], [26].

The mechanism of a DSSC is divided into several steps. The mechanism of DSSC is shown in fig. These steps are the key operating steps of a DSSC-

- **Excitation of dye-** When sunlight falls on a transparent TCO plate and reaches the dye, the electrons from HOMO get excited to LUMO due to the absorption of photons.
- **Ejection and transportation of electrons-**The dye-excited electrons were expelled into the TiO_2 semiconductor's conduction band, resulting in the oxidation of dye—electrons from semiconductor anode transport to counter electrode.
- **Reduction of electrolyte-** Electron transports to counter electrodes get captured by the electrolyte. i.e., reduction of electrolyte occurs.

- **Regeneration of dye-** The oxidized dye accepts electrons from the electrolyte and gets into its original state [21], [24].

Selecting parameters while using DSSC

There are various parameters by which the working of DSSC is optimized. These are as follows-

- **Short circuit current density (Jsc)-** It is the current per unit area that DSSC produces at no load conditions. It increases with an increase in the number of photons, i.e., the intensity of light. Unit of Jsc is mA/cm^2.
- **Open circuit voltage (Voc)-** It is generally the quantity of forwarding bias on the solar cell. It is the maximum voltage obtained at the two terminals of a solar cell when the current is zero. The Voc unit is volts (V).
- **Maximum power -** It is the product of short circuit current density and open circuit voltage. Unit is W/m^2. It can be expressed as-

$$\mathbf{P_{max} = J_{max} * V_{max}}$$

- **Fill factor-** It is defined as the ratio of P_{max} to the product of short-circuit current density and open-circuit voltage. It is expressed as-

$$FF=\frac{Pmax}{Jsc*Voc}$$

- **Efficiency-** It is the parameter that depends upon the intensity of incident light and temperature of the solar cell. It can be formulated as the ratio of ($P_{max)}$ to the incident power ($P_{in)}$.

$$\eta=\frac{Isc*Voc*FF}{Pin}$$ [31], [32].

Selecting parameters for sensitizer

The following are properties of a Sensitizer in DSSC for optimum performance [33]– [35].

HOMO-LUMO energy levels-In order to obtain an efficient electron ejection, the HOMO, LUMO energy levels of photosensitizer plays an essential role in DSSC. The HOMO-LUMO energy levels are obtained by using cyclic-voltammetry in which there are three- electrodes a working, a counter, and a reference electrode. For effective electron ejection, the LUMO energy level of the dye must be greater than the conduction band of the TiO_2, and the HOMO energy level must be less than the redox potential of the electrolyte [10],[11].

The molar extinction coefficient of dye- The molar extension coefficient is the intrinsic property of dyes that depends upon the chemical structure and composition. It measures how strongly a dye absorbs light at a particular wavelength for natural dyes. It is generally denoted by 'Ɛ.'

$$\boldsymbol{\varepsilon} = \frac{A}{L'C}$$

A= The amount of light that the sample absorbs for a particular wavelength

L’= Distance that light travels through the dye solution

C = Concentration of the dye solution

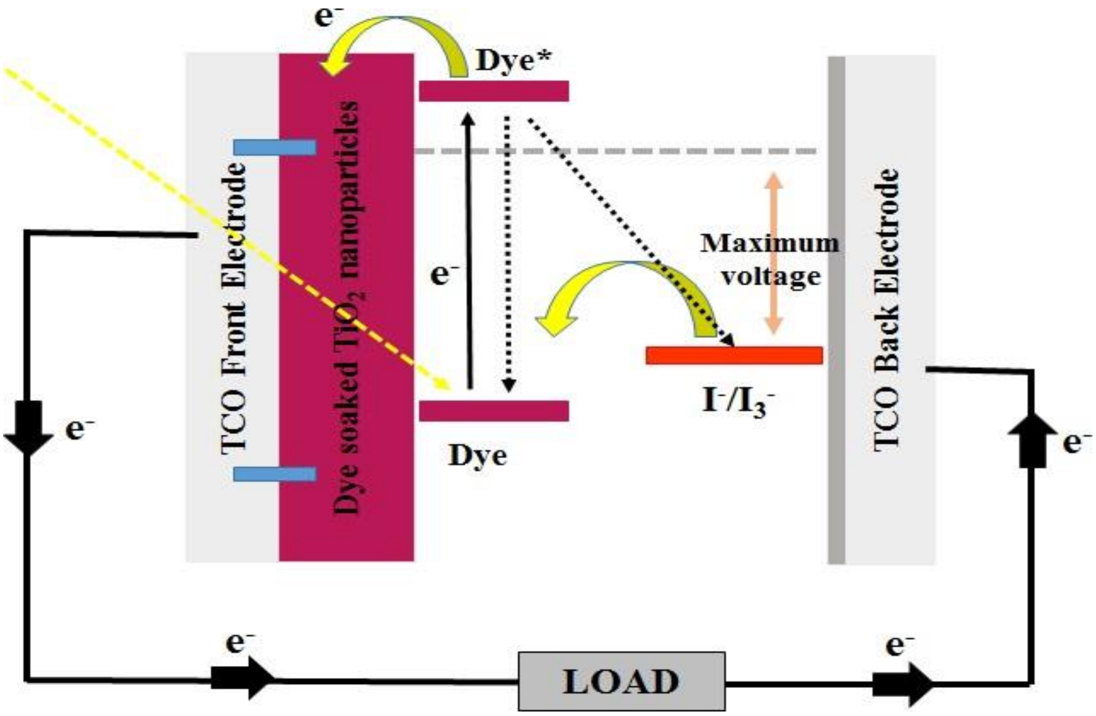

Fig.5: Energy level diagram of DSSC

Absorption of solar light- For the dye to be effective, it should absorb solar light, and the absorption spectrum of dyes should cover a broad spectrum of light.

Adsorption of dye on semiconductors- For a DSSC to be effective and efficient, there is an effective adsorption of dye on semiconductors for proper movement of electrons. Generally, in dyes that contain hydroxyl or carbonyl groups, the structure is easily chemisorbed on the semiconductor surface providing a better path for the movement of electrons.

Good photostability- In the dye-sensitized solar cell, dyes as a photo-sensitizer, degrade due to natural aging and exposure to solar irradiation, which leads to decrement in the performance of DSSC [14].

Hamper recombination losses- In DSSC, there is a recombination of ejected electrons through oxidized dye and the electrolyte. Recombination reduces the output power of DSSC and lowers the efficiency of the dye.

2.2 Optimization and overcoming challenges of fabrication steps

2.2.1 Coating methods

Coating of semiconductor film (TiO_2, ZnO, Al_2O_3, V_2O_5, etc.) on transparent conducting glass substrate (FTO/ITO) is done by many methods [36] like doctor’s blade method [37], screen printing method [38], dip coating method [39], spin coating method [40]–[43], sputtering method

[44], [45], pulsed laser deposition [46] method. The spin coating method is chosen over the conventional doctor's blade method because of the uniformity and reproducibility of the film. Film thickness and roughness can be controlled easily via the spin coating method.

2.2.2 Compact layer coating and its material

An aqueous solution of $TiCl_4$ is mainly reported in the literature for compact layer coating material. Aqueous $TiCl_4$ solution is coated by dipping FTO/ITO in the solution and then heating it till the solution color becomes cloudy for around 30 minutes [47]. Titanium isopropoxide (TTIP) and titanium isobutoxide (TTIB) in ethanol are also used to coat compact layers either by sputtering [48]–[50] or spin coating followed by sintering [51], [52]. Spin coating of TTIP solution followed by sintering is preferred over conventional methods for compact layer coating. This is due to efficient control over the thickness of the compact layer and ease of preparing compact layer solution. The need and significance of compact layers are discussed in the performance of DSSC in literature [47]. To avoid direct contact of electrolytes with FTO, a compact layer is important [49], [53].

2.2.3 Dye desorption challenge

To achieve high DSSC efficiency, it is necessary to stop dye desorption from the anode after adding the electrolyte to the cell assembly [54]–[56]. Although dye desorption is an obvious issue in DSSC, little work has been done in this area. To stop dye desorption from anodes, researchers have added co-adsorbents such as azobenzene carboxylic acid [55] and chenodeoxycholic acid [56], [57] to dye solutions. G. Pawel et. al added dye molecules in an electrolyte to address the dye desorption challenge [54]. Dye desorption was observed in every DSSC fabrication and thus efficiency was reduced greatly for every DSSC. Adding dye to electrolytes is a simple yet effective way to stop dye desorption. Hence dye desorption issues can be permanently removed from DSSC.

2.2.4 Effect of thickness transparent layer

The thickness of the dye-adsorbing semiconductor layer is crucial for achieving the best possible DSSC performance [58]. The thickness of transparent layer coatings is optimized for DSSC [43], [59]. In the literature, transparent layers ranged in thickness from 50 nm to 25μm [38], [58]–[62]. S. Prabhakaran et. al obtained the highest efficiency of 5.93 % at 10μm of TiO_2 film thickness [61]. M. Kaiswariah et. al got 2.77% of DSSC efficiency with 18.41μm thick ZnO film [59]. The thickness of the transparent layer must be optimized because it is the layer where all dye adsorbs. And no. of dye molecules is responsible for generating no. electron-hole pair.

2.2.5 Effect of temperature of anode and cell assembly

The performance of the DSSC is significantly impacted by anode and cell assembly temperature [63]–[65]. Anode temperature before dye soaking and cell assembly before electrolyte filling are steps when there is a high likelihood that deposited dye will come into contact with moisture from the environment [65]–[69]. Due to environmental moisture absorption, dye degrades. Thus, DSSC's performance suffers significantly [70]. Hung Lin Lu et. al. found that the energy-conversion efficiencies decreased with increasing amounts of isotopic water up to 10 vol% [70]. M.Y.A. Rahman et. al varied dye dipping temperatures from 30˚C to 80˚C. They found highest efficiency of 1.35% at 50˚C [71]. Sonia R. Raga et. al. soaked anode at 40˚C, assembled cell at 95˚C. They also studied the effect of cell temperature during IV measurement [72]. A similar IV study of cells at elevated temperatures was conducted by Ji Hoon Kim et. al [73]. S. Frederic et. al studied that by lowering dye adsorption temperature, recombination resistance increases [66]. P. Tika et. Al found an optimum temperature of 50˚C for soaking of anode in dye [74]. To avoid moisture interaction with dye, the temperature of the anode and cell assembly should be adjusted accordingly.

2.3 Synthesis of graphene and its application

Graphene can be used as counter electrode material, can be added in electrolyte, and can be added in anode material of DSSC. Graphene offers alternate electrical path due its high electrical conductivity. Also, graphene is cheaper. This makes graphene a suitable material to be used in DSSC.

2.3.1 Synthesis of graphene

Graphene, two-dimensional covalently bonded carbon atoms arranged in a hexagonal ‘‘honeycomb’’ lattice structure, a rapidly rising star in nanomaterial research, has garnered significant interest due to its unique combination of exceptional mechanical, electrical, and thermal properties [75]. Its high in-plane strength, measured by atomic force microscopy, is around 1 TPa [76]. In addition to its remarkable mechanical properties, graphene exhibits excellent thermal conductivity, surpassing that of any other material, and high electrical conductivity due to the presence of delocalized π-electrons [77]. As the thinnest 2D material, graphene possesses a high carrier mobility (>200 000 $cm^2 V^{-1}s^{-1}$) [78], high electron density (4 x 10^{-9} cm^{-2}) [79], high specific surface area (2600 $m^2 g^{-1}$) [80], high optical transparency (97.7%) [81], [82]and strong catalytic activity. These exceptional properties make graphene a promising material for numerous applications in various fields, including electronics, sensors, catalysis, energy storage, and composites. However, the widespread use of graphene is limited by the difficulty of synthesizing high-quality graphene in large quantities [83]. In recent years, various techniques have been established for graphene synthesis, including mechanical exfoliation, chemical vapor deposition (CVD), epitaxial growth, chemical reduction, and liquid-phase exfoliation [84], [85]. The most used methods for the large-scale production of graphene are CVD and liquid-phase exfoliation.

CVD is a promising method for the scalable production of high-quality graphene films. In this method, a gaseous precursor containing carbon is introduced into a high-temperature furnace, where it decomposes and forms graphene on a metal substrate. CVD graphene exhibits excellent properties, including high carrier mobility, low sheet resistance, and excellent thermal stability [77]. However, the scalability of CVD is limited by the size of the furnace and the cost of the substrate.

Liquid-phase exfoliation is another promising method for the large-scale production of graphene. This method involves the dispersion of graphite in a solvent with the aid of a surfactant or a reducing agent, followed by exfoliation into individual graphene sheets using sonication or other mechanical means [86]. The liquid-phase exfoliation method can produce high-quality graphene with fewer defects and high dispersibility, making it an attractive method for various applications [87]. Additionally, liquid-phase exfoliation can be used to produce graphene in a range of solvents, providing flexibility in material processing [88]. The liquid medium can be either polar or nonpolar, and the choice of liquid affects the quality of the resulting graphene [88]. Commonly used polar solvents include water, ethanol, and dimethylformamide (DMF) [89]. Nonpolar solvents, such as chloroform, toluene, and N-methyl-2-pyrrolidone (NMP), have also been used for liquid exfoliation [90]. The choice of liquid medium affects the thickness, lateral size, and quality of the graphene produced [91]. For example, graphene produced using DMF has been shown to have a smaller lateral size and higher quality compared to graphene produced using water [92]. Liquid exfoliation can also be used to produce functionalized graphene, which has a variety of potential applications in biomedicine, electronics, and energy [93]. Functionalization involves attaching chemical functional groups to the surface of graphene, which can enhance its solubility, biocompatibility, and electronic properties [94]. Commonly used functionalization agents include amino acids, surfactants, and polymers [95] Reducing agents play a crucial role in the synthesis of graphene by chemical reduction of graphene oxide which involves the reduction of graphene oxide to graphene by a reducing agent. Graphene reduction process involves removal of oxygen function group graphene oxide to restore the sp^2 hybridization of the carbon atoms network [96], leading to the formation of graphene. The choice of reducing agent plays a vital role in determining the properties of the resulting graphene, including its electrical conductivity, surface chemistry, defect density, andthe quality of the resulting graphene. Several reducing agents have been reported for the reduction of graphene oxide, commonly used reducing agents include hydrazine [97], [98], sodium borohydride [99], [100], KOH [101], ascorbic acid [102], [103] and green reducing agents [104].

This work comprehensively focuses on the study and synthesis of graphene using two approaches: physical exfoliation (Liquid exfoliation) and chemical exfoliation (oxidation-Reduction) methods and combining these two approaches. In this work, graphene was synthesized via both the exfoliation methods along a new combined exfoliation method.Based on introducing physical exfoliation at different chemical exfoliationsteps, 3 variations of RGO are synthesized. Physical exfoliation is added before oxidation, during oxidation, before reduction, and during reductionsteps in the chemical exfoliation method to combine these two methods. FESEM-EDAX, XRD, Raman spectroscopy, TEM, EIS, Particle size-ZetaPotential, and UV visible absorption characterization techniques are used to study synthesized materials.

2.3.2 Graphene as counter electrode

A typical DSSC consists of a nanocrystalline semiconductor oxide mostly titanium dioxide nanoparticles, a dye that absorbs sunlight like the chlorophyll in green leaves, an electrolyte redox couple, and a catalyst material as cathode, also called a counter electrode (CE). As a crucial component in DSSCs, the main functions of a CE are to transport electrons from external circuits and catalyze the reduction reaction of I_3^- to I^- for dye regeneration. The Overall I_3^- reduction reaction occurring on the CE surface can be described in (1). Reaction (1) can be divided into the following steps (as depicted in (2)– (5)) involved in the reduction mechanism I_3^- :

$$I_3^- + 2e^- \longleftrightarrow 3I^- \quad \text{.......} (1)$$

$$I3^- \longleftrightarrow I_2 + I^- \quad \text{.......} (2)$$

$$I_2 + 2CE \longleftrightarrow I(CE) + I(CE). \quad \text{.......} (3)$$

$$I(CE) + e^- \longleftrightarrow I^-(CE). \quad \text{.......} (4)$$

$$I^-(CE) \longleftrightarrow I^- + CE \quad \text{.......} (5)$$

Reaction (2) represents the solution phase reaction, which has been verified to be relatively fast and considered to be in equilibrium. Then I_2 Dissociates into two surface I atoms upon adsorption on the CE surface (designated as I (CE)) via (3), and subsequently, I atoms on the CE surface are reduced to I^- ions adsorbed on the CE surface through one-electron transfer as depicted in (4). After that, the adsorbed I^- ions are desorbed from the CE surface to be the solvated ions in the electrolyte as illustrated in (5). Based on the functions of a CE and the reduction mechanism of I_3^- , an efficient CE should exhibit both high electrical conductivity and electrocatalytic activity to keep a low overpotential and minimize energy loss in DSSCs. Since their initial invention, dye-sensitized solar cells (DSSCs) have offered cost-effective photovoltaic systems. DSSCs generally employ Pt nanoparticles for CE material due to their high electrical conductivity and excellent electrocatalytic activity along with high electrochemical stability.

However, Pt is expensive, rare, and already widely in demand as a catalyst in various fields, and the high cost of Pt (ca. $50,000/Kg) restricts its large commercial applications. Therefore, much effort has been devoted to exploring efficient Pt-free CEs [75]. To date, a great deal of materials is attracting attention in the development of DSSCs including carbon materials, conducting polymers, and inorganic materials have been introduced as alternative CE materials to Pt. Graphene, two-dimensional covalently bonded carbon atoms arranged in hexagonal ‘‘honeycomb’’ lattice structure, is a rapidly rising star nanomaterial research [105]. As the thinnest 2D material, graphene possesses a high carrier mobility (>200000cm^{2}V^{-1}s^{-1}) [106], [107], high electron density (4x10-9 cm-2) [108], high specific surface area (2600m^{2}g^{-1}) [109], [110], high optical transparency (97.7%) [82], [111]–[113], and strong catalytic activity [114], [115]. These properties have stimulated the extensive exploration of graphene for use as a counter electrode and as an electronic promoter for DSSCs [108], [116]. Recently researchers have done massive research on developing graphene-based counter electrodes [82], [116], [117]. Man-Ning lu et. al briefly describe the structure and benefits of each graphene-based material and offer potential approaches for building new graphene-based catalysts in future research for high-performance and affordable DSSCs [117]. M. S. Mohamed et. al used a modified Hummers' process to create SnO_2-decorated graphene oxide (SnO_2/GO), which was then chemically coated with SnO_2 nanoparticles. The nanocomposite was then utilized in a dye-sensitized solar cell (DSSC) as a non-precious counter electrode with an enhanced efficiency of 4.57% [118]. Cheng-En Cheng used Pt/Graphene as a counter electrode in DSSC [119]. Nguyen Huu Hieu et. al studied graphene-based materials in the fabrication of DSSC like

ZnO-Graphene as anode, graphene, and Pt-graphene as cathode in DSSC [120]. Similarly many researchers have used graphene as counter electrode material in DSSC to reduce cost and improve the efficiency of DSSC [121]–[126],[117]–[120]. In this work, we comprehensively focus on the investigation of graphene-based counter electrodes for Pt-free DSSCs by different routes of synthesis namely the physical exfoliation method, chemical exfoliation, and combined exfoliation method.

2.3.3 Graphene liquid electrolyte

For use in dye-sensitized solar cells (DSSC), a graphene oxide sponge (GOS) is created and used as a nanofiller (NF) of an iodide liquid electrolyte. The conductivity of the electrolyte and the functionality of the DSSCs are examined as a function of GOS NF concentration. According to the findings, adding GOS NFs significantly improves the liquid electrolyte's conductivity [127], [128]. In this work, novel electrolytes for dye-sensitized solar cells (DSSCs) were made using two-dimensional graphene flakes. To create novel electrolytes, minute amounts (up to 3 weight percent) of graphene nanoflakes were suspended in the ionic liquid (IL) 1-propyl-3-methylimidazolium iodide (PMII). The solar cell efficiency was increased by more than 25 times because of using these electrolytes in DSSCs [129]. Due to graphene's excellent electron mobility, graphene nanosheets (GNs) were introduced to liquid electrolytes in this work to raise their electric conductivity and boost the effectiveness of dye-sensitive solar cells (DSSCs). In particular, the efficiency of the DSSC device using the 20-mg graphene electrolyte solution was the greatest (9.26%), 20% greater than the efficiency of the device using the non-graphene electrolyte solution [130]. In this work, graphene with the least charge transfer resistance was added to the liquid electrolyte in two mass ratios and was used in DSSC fabrication. An optimum graphene ratio was obtained, and JV characteristics were studied.

2.4 Gel electrolyte

Pujiarti et al. (2018) investigated a polymer gel electrolyte containing an ionic liquid in organ siloxane polymer gels. Efficiency of 5.67% and a high open-circuit voltage of 0.73 V was reported [133]. Jauhari et al. (2018) investigated the use of a polyaniline/thiourea matrix for solid-state dye-sensitized solar cells (DSSCs). The optimized electrolyte showedimproved efficiency [134]. Wang et al. (2002) used an ionic liquid polymer gel electrolyte containing 1-methyl-3- propyl imidazolium iodide (MPII) and poly(vinylidenefluoride-cohexafluoropropylene) (PVDF–HFP) as aquasi-solid-state electrolyte in dye-sensitized nanocrystalline TiO_2 solar cells. The resulting cells showed an overall conversion efficiency of 5.3%

[135]. Yang et al. (2012) discusses the development of a novel composite polysaccharide/inorganic oxide electrolyte for high efficiency quasi-solid-state DSSC [136]. Susan, M. A., et al. (2005) presents a new methodology for highly conductive polymer electrolytes by polymerizing methyl methacrylate (MMA) in 1-ethyl-3-methyl imidazolium bis (trifluoromethane sulfonyl) imide (EMITFSI) in the presence of a small amount of a cross-linker [137]. Yogananda, et al. (2017) developed an eco-friendly electrolyte for DSSCs by using rice starch as the biopolymer gel electrolyte, which is a cheap and abundant source of biopolymer, and Lithium iodide as the salt [138]. Perera and Vidanapathirana (2017) aimed to optimize the composition of a gel polymer electrolyte for use in DSSC applications consisting of 100 PVdF / 400 EC / 400 PC / 150 Hex4NI /7.3 I_2 exhibited the highest conductivity of 3.43 x 10-3 Scm^{-1} [139]. Li.et.al (2010) presents a novel gel polymer electrolyte based on poly(acrylic acid-g- gelatin)/polypyrrole that has high conductivity and catalytic function for I^-/I_3^- redox reaction[140]. Tiautit et al. (2014) studied polymer gel electrolytes (PGE) of PVDF-HFP/PVA blends. The study used a fixed concentration of polymer blend at 10 wt%[141]. Khanmirzaei, M. H. et al. (2015) used polymer electrolyte based DSSC with rice starch and 1-methyl-3-propylimidazolium iodide ionic liquid. The highest ionic conductivity of 1.20 × 10−3 S cm^{-1} was achieved upon addition of 20 wt.%

of MPII ionic liquid. The highest energy conversion efficiency of 2.09% was attained after the addition of 20 wt.% of MPII ionic liquid [142]. Illa, S. and Basak, P. (2018) developed a polymer electrolyte integrated DSSC endow enhanced stability. The resulting cells showed an efficiency of 2.2% with a short-circuit current density of 4.3 mA and an open-circuit voltage of 0.76V [143].

2.5 Research gap

In DSSC Fabrication, compact layer coating is crucial steps as its proper coating ensures no short circuit in the cell. $TiCl_4$ is mostly used for compact layer coating, which is highly reactive chemical. Here, compact layer coating solution is made with TTIP. Coating of absorber and diffused layer. Doctor's Blade Method is generally used, whichdo not give control over thickness and uniformity. In this work, spin coating method is used for coating layers. Thickness of absorber layer vary from literature to literature. Therefore, DSSC is fabricated with 3 different thickness of absorber layer. And performance of DSSC is calculated to ensure optimized thickness. Dye desorption is fast and evident process. This issue is not discussed and generally use of co-adsorbent is suggested. Here, 'addition of dye in electrolyte' simple method is used to address dye desorption issue.

Graphene is a versatile material with high electrical conductivity. It can be used as cathode material, electrolyte additive, anode material additive. Therefore, graphene is synthesized in this work. Role of Exfoliation to synthesize graphene is not discussed much inliterature. Here, emphasis is put on exfoliation effect on quality of graphene. Quality of graphene by physical exfoliation method is equally good. Therefore, DSSC is fabricated with both chemically and physically exfoliated graphene. Very few literatures are present which uses graphene in liquidelectrolyte to further improve its conductivity. Here, graphene is added to electrolyte.

Very few literatures showed plant based, biodegradable gel electrolyte DSSC with efficiency > 5%. Plant based gel electrolyte lasting for long periods are not mentioned inliterature much. Here agar-agar-based gel DSSC is fabricated. Dye desorption issue is not discussed anywhere in literature for gel DSSC. Dye desorption issue of gel DSSC is addressed in this work.