The latest trends in synthesis of dye-sensitized solar cells

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Abstract. This rapid consumption and depletion fossil fuels has catalyzed the need for shifting into renewable energy like wind energy, solar energy and tidal energy. One of the most widely used methods is harvesting energy from the sun for use in semiconducting material. For this purpose, photovoltaic (PV) cell also called as solar cells are used. The various trends in the dye sensitized solar cells were discussed with the changes made in photoanode, counter electrode and the redox electrolyte. Especially, graphene materials in the dye-sensitised solar cells is focussed in this review article.

Keywords: Dye-sensitized solar cells, graphene materials, photoanode, electrolyte and counter electrode.

1. Introduction
The beginning of 21st century saw a major growth in the field of science and technology. Consumption of hydrocarbon fossil fuels like coal, oil and natural gas was increased drastically. Various problems like greenhouse effect and global warming was the consequence. Solar energy is one of the cheapest, cleanest and safest renewable energy in the world. PV devices are generally classified as first, second and third-generation solar cell. First generation solar cell primarily comprised of thin silicon wafers with performance about 15-20% [1]. They are the most widely used solar cell today. Second generation solar cell consist of thin film solar cell like: amorphous silicon, cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS). Their performance varies between 10-15% [1]. The third-generation solar cell are made up of materials like: nanotubes, silicon wire, organic dyes. The third-generation solar cells are in working stage and not available commercially. In this article, we discuss various graphene based solar cells. Graphene have been an extensive field of study by chemist, physicists and engineers [2]. Replacing different types of atoms (N, B, S and P) with carbon in graphene improves its conductivity and electrochemical properties of graphene [3-5]. One of such solar cell is graphene-based dye sensitized solar cell. It is a third-generation solar cell. It has less manufacturing cost, high power conversion efficiency and wide spectral response in visible light region for various indoor activities [6].

Graphene, a sp²-hybridised carbon allotrope is a 2D atomically thin single layer of 3D graphite material. Figure 1 shows the structure of graphene. It is quite popular due to its numerous extraordinary properties like: large specific area (2630 m² g⁻¹), high Young's modulus (~1.0 TPa), high thermal conductivity (~5000 W m⁻¹ K⁻¹) [7]. Still graphene cannot be used directly for solution-processed application like sensors, batteries and solar cells. With this, the focus is gradually shifted to new solution-processable graphene derivatives. The chemically derived form of graphene oxide (figure 2) was also explored [8].
Although the graphene oxide (GO) obtained is insulating so it is reduced to form the resulting reduced graphene oxide (rGO). The removal of oxygen from the GO reduces the stability, but several new methods have been found out to overcome the problem.

![Graphene](image)

**Figure 1.** Structure of graphene

2. **Dye sensitized solar cells**

Since the cost of dye-sensitized solar cells (DSSCs) is less it has become a promising field since their discovery in 1991 [9]. The main purpose of such solar cell is that they use specialized material for their specific functions of charge separation, charge absorption and proton transport. DSSCs are cost effective as compared to standard silicon solar cells as the cost of materials is less. Their fabrication is easy as DSSCs are not affected by environmental contaminants, synthesized at lower temperature and the manufacturing method for printing the DSSCs is quite low. Also, DSSCs function properly in conditions like: dusk, dawn and in cloudy conditions. These capabilities of using diffused light increases their usage more widely for various applications in windows and sunroof. DSSCs are also known as Grätzel solar cells in the name of their inventor Michael Grätzel at Swiss Federal Institute of Technology in Switzerland.

A systematic representation of dye-sensitized solar cell is given in figure.1 [10]. DSSCs have four major components like:

- A photoelectrode using mesoporous oxide layer such as TiO$_2$.
- A dye-sensitizer covalently bonded to TiO$_2$ layer for generation of photo-excited electrons.
- An electrolyte having redox couple (iodide/triiodide) in an organic solvent such as solid electrolyte.
- A counter electrode for the electrochemical reaction which is made up of platinum coated conductive glass substrate.
Dye sensitizers on the solar cell gets activated when sunlight strikes it. In this process, the TiO$_2$ film is activated and the electrons are introduced to conduction band of TiO$_2$. These injected electrons then get diffused past the mesoporous film reaching the anode and do the useful work. The cycle gets completed when the electrons are received by the electrolyte at counter electrode and regenerates the dye sensitizer.

The power conversion efficiency (PCE) of DSSCs are affected by various parameters including the photocurrent density. So new dye-sensitive materials and electrolytes have been attempted to improve the photovoltaic efficiency of DSSCs. Hara and Arakawa [11] found different components and operating principles of DSSCs. The four-energy level of the DSSC are: the excited state, the ground state, and the fermi level of TiO$_2$ electrode and the redox potential of the iodide/triiodide present at the electrolyte. Basic operating principle of this process is photosensitization. In this the photosensitized dye absorbed on TiO$_2$ absorbs photons from sunlight thus exciting the dye molecule. Then the electron from photoexcited dye are injected to conduction band of TiO$_2$ which causes oxidation. These oxidised dye molecules attain ground state after accepting electron from iodide/triiodide redox couple. The newly formed oxidised triiodide moves to the platinum counter electrode and gets reduced to iodide ion. The main disadvantage is the corrosive nature of the redox electrolyte, the stability of the electrolyte, and its toxicity.

2.1 Photoanode

A semiconducting layer generally TiO$_2$ which is dye sensitized with conducting substrate like glass or plastic is used as the photoanode of DSSCs. A typical photoanode of DSSC is composed of three sections: a transparent electrode, a semiconducting layer, and the sensitizer itself. Our focus is in the use of graphene as photoanode.

2.1.1 Transparent Electrode

DSSCs has it use in both frontside and backside illumination. For frontside illumination in DSSC substrate side of the device is taken as the light source, whereas for backside illumination electrolyte is taken as the light source. So, for this purpose an electrode having greater transparency is needed for backside illumination. These transparent electrodes find their use in flat panel displays and touchscreens. The commonly used transparent electrode is Indium tin oxide (ITO). The problem with this electrode is that indium is a rarely found metal, moreover ITO electrodes produced have brittle properties and are less compatible with strong acid, and are less stable at high temperature [12]. An alternate to ITO is
fluorine-doped tin oxide (FTO), which is cheaper than ITO but the films made of FTO have high resistivity per optical resolution, 15 Ω/sq at T ~85% [13]. High optical transparency and low sheet resistance are two of the most important criteria needed while selecting electrode for DSSC. For reducing problems related to cost and performance limitation of the transparent electrode research on new material is going on. Properties like high electron mobility and transparency makes graphene a suitable candidate for replacing conductive oxide. Using pristine graphene as a material for transparent electrode is still unlikely as it would not meet the industrial target, still electronically doped graphene material along with graphene-metal hybrids are having greater scope to be used as transparent electrode [14-18].

Graphene and its composites form a suitable replacement for various other electrodes considering their property of high transparency and good electrocatalytic activity. The first reported fabrication of graphene and its use as transparent electrode for DSSCs was done by Wang et al. in the year 2008. The graphene films were produced by exfoliating the graphene oxide and then thermally reducing the platelets formed [19]. The developed film was used as a window electrode having wavelength range between 1000-3000 nm, and conductivity of 500 S cm-1 and transparency greater than 70%. This work showed future scope of graphene to be used as transparent electrode. Zhao et al. found high porosity and large specific surface area by using graphene and titanium film electrodes to promote adsorption rate of sensitizing dye [20]. The PCE for this electrode was found to be 7.52%. Lee et al. used graphene having monolayer with TiO₂ as photoanode. There was an increase of 31% in PCE over that of a TiO₂ anode [21]. Huang et al. prepared graphene films on SiO₂ substrates. This material has reached a photovoltaic efficiency of 4.25%, these values are comparable to FTO used as electrodes [22]. The results found gives the future application of graphene films in transparent electrode. But it would be more suitable if there is further improvement in the cost and the technology of the material.

2.1.2 Semiconducting Layer
Several losses occur when an electron which is photoexcited gets injected from dye to the semiconductor diffusing with the current collector. The major loss happens due recombination of injected electron with oxidised species of redox couple. Various techniques have been developed to reduce these losses. Like, anatase phase of TiO₂ has energy levels which helps in achieving unity injection efficiency with acceptable voltage drop [23-25]. Even the conductivity of TiO₂ is quite high because of photoexcitation of electron and due to oxygen vacancy n-doping [26-28]. Crack free and sintered films that are ideally for DSSCs can help in achieving good charge collectible efficiency. Thickness of the film (10-20 μm) is taken to receive sufficient light harvesting and is calculated by surface area and extinction co-efficient of dye [29-31]. Creating a DSSC with efficiency greater than 10% has been quite difficult. So, researchers have sought the use of graphene for improving the efficiency of semiconducting layer.

Kim et al. was reportedly first in using graphene material for semiconducting layer. He used photocatalytically reduced graphene oxide and TiO₂ nanoparticles which had a PCE of 5.26% [32]. But, there was a reduction in transmissivity from 85% to 78% due to light absorption from the film so this approach was not found to be beneficial. There have been various other studies which have found several other approaches with further improvements [33-34]. Chen et al. [33] improved the efficiency of DSSCs by using spin-coating graphene thus reducing charge recombination process at FTO nanoparticles and FTO/TiO₂. The PCE was found to be improved from 5.80% to 8.13% [33]. Other method to improve the efficiency of DSSC by increasing the charge collection efficiency. Yang et al. [35] and Wang et al. [36] were first to work in this topic. The advantage of this method was that graphene incorporated with TiO₂ increased the light collection and the use of photoanode forms a graphene bridge that prevents
charge recombination. These advantages made the short-circuit current density and PCE to increase by 45% and 39% [35-36].

The above obtained results give the future scope of using graphene in semiconducting layer. Research on this topic is still on its primary stages and most of the work is based on assumptions. Much work is needed in this field to show significant growth in semiconducting layer.

2.1.3 Sensitizer
The process of harvesting sunlight is done by the photosensitizing dye. Primary purpose of the sensitizer is to absorb light and transfer electron to conduction band of semiconductor. The dye needs to have a long spectral range for increasing sunlight absorption. In addition to these, the negative lowest unoccupied molecular orbit energy than the conduction band of semiconductor and more positive highest occupied molecular orbital energy than redox potential of electrolyte [37-38]. Yum et al. [39] and Mishra et al. [40] found various metal free organic dyes for DSSCs. Narayan reviewed the photosensitizers using natural dye [41]. The working of DSSCs are quite similar to the photosynthesis process in plants. Pigment chlorophyll found in the chloroplasts of the plant has similar application to the dye present in DSSCs. Recent developments in the use of graphene in sensitizer is our primary focus. Recently several researchers have found the application of graphene in photosensitizers [38]. Pristine graphene has an absorption rate of 2.3% of light for each single layer of material [42]. The most important part of graphene-based materials in DSSC sensitizer would be taking the advantage of quantum effect and use of ultrafast injection to overcome intrinsic limitation for conductive devices [43].

2.1.4 Redox electrolyte and counter electrode in DSSC
The key point in these type of solar cells is to have a high light harvesting efficiency. Two approaches are followed by most of the researchers to increase the efficiency of the cells, either by using electrodes with large surface areas. TiO$_2$ thin films are basically used because of their large surface areas and they are the most suitable to have a higher performance. This TiO$_2$ electrode is created using two techniques namely Doctor Blade technique and Screen Printing technique [11]. The electrolyte used in DSSC consist of I-/I$_3$- which mediate between the electrode and the counter electrode. The different types of electrolytes that are currently being used are polymer electrolyte, solid polymer electrolyte and gel polymer electrolyte. The most recent one being used is poly-ionic liquid polymer electrolyte. The ionic liquids can be classified as Doping of polymers with ILs, In-situ polymerization of vinyl monomers in ILs and Polymerization of polymerizable ILs.

Counter electrode is another essential part of the dye sensitised solar cell. A transparent thin graphene/PEDOT-PSS film is prepared by aqueous mixture of graphene and PEDOT-PSS. The advantage of this is we obtain the high electro catalytic activity of graphene and the high conductivity of PEDOT-PSS [44]. By doing this a high energy conversion efficiency was obtained almost 4.5%. The efficiency can be further increased by using carbon nanotubes. These carbon nanotubes are applied on the counter electrode by two methods either by screen printing and chemical vapor deposition. The efficiency of these DSSC have reached the 10% efficiency [45].

3. Conclusion
The various trends in the dye sensitized solar cells were discussed with the changes made in photoanode, counter electrode and the redox electrolyte. Though dye sensitized solar cells have a great potential in the future but still it has not been able to reach 15% but changes are being made in order to reach the
mark. Most of the work using graphene-based materials on DSSCs are at their initial stage. Use of graphene materials in DSSCs for achieving environmental stability, non-toxicity and its overall cost is a big task for industries. Graphene materials for DSSCs have a lot of scope and they are growing slowly.

4. References

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