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Graphene/Metal Oxide Nanocomposite Usage as Photoanode in Dye-Sensitized and Perovskite Solar Cells

Tahira Mahmood, Madeeha Aslam and Abdul Naeem

Abstract

Global energy shortage will be one of the most critical challenges in the next 50 years. Currently, over 80% of energy consumed is produced from fossil fuels, which is directly linked to global warming and environmental pollution issues. Environment-friendly renewable energy is rapidly gaining importance for the existence of human civilization. A leading source of renewable energy is the solar energy, which is inexhaustible and abundantly available. Solar cells that convert solar energy directly into electricity are drawing considerable attention as a potential turnkey solution to address these challenges. Several approaches have been made in this respect, including the development of better materials and the designs of new solar cell configuration and architecture. Among the innovative materials with potential application in emerging 3G solar cells, graphene and its derivatives such as GO, rGO and G/nanocomposite have been widely explored as transparent conducting electrodes, electron donor or acceptor materials and counter electrodes (CE). In this chapter, the use of graphene nanocomposites has been explored as an electrode material in DSSCs and PSCs. Recently, graphene/metal oxide nanocomposites have been widely used in DSSCs and PSCs and played a significant role in increasing charge transport, reducing charge recombination and thus enhancing the performance of solar cell.

Keywords: graphene, nanocomposite, metal oxide, photoanode, energy, DSSCs, PSCs

1. Introduction

1.1 Solar energy as an alternative of renewable energy

Energy and environmental problems such as pollution and global warming are the most outstanding challenges that humanity will face in the next 50 years. Lately, global energy demand primarily for conventional energy resources such as fossil fuel, coal and natural gas has been increasing with population growth and industrial development. Up till now, over 80% of energy consumption is met with from fossil fuels, which cause global warming and environmental pollution issues. Moreover, they are non-renewable and will ultimately be exhausted in the future.

Due to the increasing interest in renewable energy sources, imminent research is being focused towards harvesting energy from natural resources. Among the various choices, exploitation of sunlight for energy production and environmental remediation is the utmost crucial research areas of the twenty-first century.

The ultimate renewable source of energy is the sun. Sunlight is the most abundant energy source available to mankind. The sun emits a large amount of energy (approximately 32×10^{24} joules/year), which is much more than the world's whole demand. It is abundantly available, and only its 0.01% use would meet the worldwide energy necessities [1]. In this context, photovoltaic (PV) technology is considered as one of the ideal candidates, as they convert solar energy directly into electricity. Hence, effectively converting solar energy directly into electricity has been a promising solution to the energy issues [2]. From the perspective of environmental protection and energy conservation, it is required to produce electricity from solar energy by means of photovoltaic devices or solar cells.

1.2 Solar cells

Solar cells are probably the foremost contributor to fulfill the future energy requirements. Several approaches have been made for the fabrication of solar cells. Generally, solar cells are classified as first-, second- and third-generation solar cells. The first-generation (1G) solar cells are also called conventional, traditional or wafer-based cells and include silicon solar cells (polysilicon and monocrystalline) [3]. The power conversion efficiencies (PCE) of crystalline silicon solar cells have reached up to 26.6%. The SSCs with more than 90% share are presently leading the commercial photovoltaic markets. However, they are characterized by a severe preparation conditions and high cost [4, 5]. The second-generation (2G) solar cells, thin-film solar cells which include direct band gap semiconductors, were then explored. These included cadmium telluride (CdTe), gallium arsenide (GaAs), copper zinc tin sulphide (CZTS) and copper indium gallium selenide (CIGS) thin-film solar cells [4]. Though thin-film solar cells have led to reduced cost as compared to silicon solar cell, they require high-temperature and vacuum vapor deposition processes. Furthermore, they mostly contain toxic and rare elements, thus limiting their widespread applications [6, 7]. To overcome these challenges, third-generation (3G) solution-processed solar cells have been developed, which include organic solar cells (OSCs), quantum dot-sensitized solar cells (QDSCs), dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs) [8]. Several PV technologies are under continuous development to meet the world demand for energy; in this chapter, however, we will focus our discussion in the emerging PV devices, i.e. dye-sensitized solar cells and perovskite solar cells.

The solar cell performance can be measured by its power conversion efficiency (PCE), cost and stability. Solar cell efficiency is the “measure of its output power per unit intensity of the incident light”. The basic measurement to control solar cell efficiency is current (I) and potential (V) measured over an external resistance and at incident light intensity. The I-V characteristics can be produced using a Keithley SourceMeter SMU instrument. The I-V measurements were carried out to get significant knowledge about parameters of the solar cell for cell's performance. The typical illumination condition used for measurement of solar cell is 100 mW. cm^{-2} (intensity of incident light), which is recognized as one sun or air mass (AM) 1.5. It is the sunlight that reaches the earth's surface through air mass at 42.8° angle. In laboratories, a solar simulator attains this standard illumination condition [9]. The photovoltaic parameters thus calculated are open-circuit voltage (VOC), short circuit current (I_{SC}), fill factor (FF) and power conversion efficiency. In 2016, the

power conversion efficiency values certified by the National Renewable Energy Laboratory (NREL), the best research dye-sensitized solar cell, organic photovoltaic cell (OPV) and the perovskite solar cell, are 11.9, 11.5 and 22.1%, respectively [10].

1.3 Graphene oxide

Exploring innovative materials with tailored nanostructures and desired properties for energy application is a recent research area. To this end, graphene has distinguishing advantages over conventional nanomaterials, and substantial efforts have been made to utilize its valuable features for efficient energy devices. Carbon nanomaterials such as graphene and CNTs due to their abundance, low cost, good electrical conductivity and high chemical stability have been applied in 3G solar cells [11, 12].

Graphene is a single thick sheet of sp^2 -hybridized carbon atoms organized in a hexagonal lattice [13]. Graphene, first discovered in 2004, has appeared as a rising star in material engineering. Geim and Novoselov winner of Nobel Prize in 2010 opened infinite new possibilities for graphene, and recently, around the world many efforts have been made to present graphene-related materials to many industries [14]. Graphene has extraordinary properties such as high electrical conductivity (108 S/m), good thermal conductivity (5000 W/mK), high surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) and electron mobility ($250,000 \text{ cm}^2/\text{VS}$), excellent mechanical strength, room temperature quantum hall effect, tunable band gap and good biocompatibility [15, 16]. Graphene is extremely optically transparent material having absorption ($<2.3\%$), transmittance (over 97.7%) and insignificant reflectance ($<0.1\%$) [11].

Due to these interesting properties, graphene, GO and rGO have attracted increased popularity for the use in optoelectronic (LEDs, photodetectors, touch screens, etc.), energy conversion (photocatalytic water splitting, photoelectrochemical (PEC) water splitting and photovoltaic cells), energy storage devices (batteries and capacitors) and environmental applications (gas sensors, photocatalytic degradation of pollutants and heavy metal removal) [17–19].

Geim and coworkers first isolated a 2D single layer of graphene from graphite by peel-off method in 2004 at Manchester University, named as Scotch tape method [20]. This led to an explosion of interest, and several studies have been carried out on the structure and properties of GO. Therefore, a series of approaches have been used to obtain a high-quality and large surface area graphene oxide. These approaches are classified into two main types: the bottom-up and the top-down.

1.3.1 The bottom-up

The bottom-up approach is simple and is exfoliation of a graphene layer from a graphite. However, it requires high temperature and produces graphene with comparatively more defects than the top-down approach. Chemical vapor deposition (CVD), epitaxial growth on single-crystal SiC and carbonization are the representative bottom-up methods. CVD is a distinctive method used to synthesize large-area graphene sheets on metal foil substrates [20–22]. However, due to complexity, high temperature and cost of metal substrates, these methods are not widely used [22].

1.3.2 Top-down

The top-down method involves the formation of graphene oxide using carbon-based materials. The top-down method has advantages like high yield, ease of

operation and solution-based processability [12, 23]. This approach involves the chemical exfoliation of graphite, thermal exfoliation, electrochemical exfoliation and chemical reduction strategy. The typical method used for synthesis of GO was developed by Hummer and coworkers, which involves oxidation of graphite by sulfuric acid and potassium permanganate [18, 20].

Graphene oxide (GO) is the important derivative of graphene, which can be synthesized directly from graphite oxide. GO comprises of a 2D network of sp^2 - and sp^3 -bonded C atoms. The exceptional atomic and electronic structure of GO opens opportunities for new functionalities. GO is a highly oxidized graphene sheet containing many oxygen-comprising functional groups like carboxylic acid, hydroxyl, epoxide and carbonyl groups. Due to the presence of these oxygen-containing functional groups, graphene oxide is easily dispersible in water and other organic solvents [16, 23]. These functional groups are outstanding reactive sites for various functionalization reactions, nucleation and growth of nanoparticles [24]. Reduced graphene oxide (rGO) is an intermediate phase of GO and graphene, possessing various oxygen-containing functional groups and lattice surface defects which cause the electrocatalytic site in metal nanoparticles. Therefore, rGO exhibited better performance than the fully reduced defect-free graphene [12].

GO acts as semiconductor having band gap of 1.7 eV at room temperature. GO is an ambipolar material because it can act both as n- and p-type conductors. Therefore, they can be used both as ETL and HTL, depending upon the oxygen-containing functional groups in their structure. Graphene oxide, due to its unique structure and properties, has shown many advantages over rare metals, fluorine-doped tin oxide (FTO) and indium tin oxide (ITO) in optoelectronics such as solar cells and light-emitting diodes as shown in **Figure 1** [12, 15, 25].

Graphene oxide tends to agglomerate because of van der Waals interaction between the graphene layers, preventing its application in several fields, though this drawback can be avoided by hybridizing graphene with CNTs, metal oxides and polymers [11]. To further explore the potential application of graphene-based materials, graphene nanocomposites are attracting more and more interest (**Figure 2**).

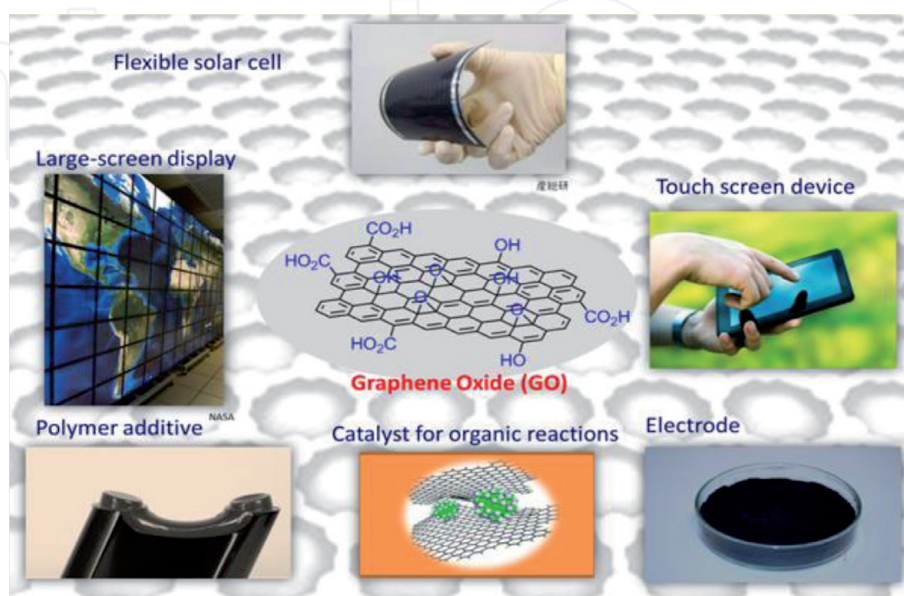


Figure 1. Applications of graphene oxide in electronics.

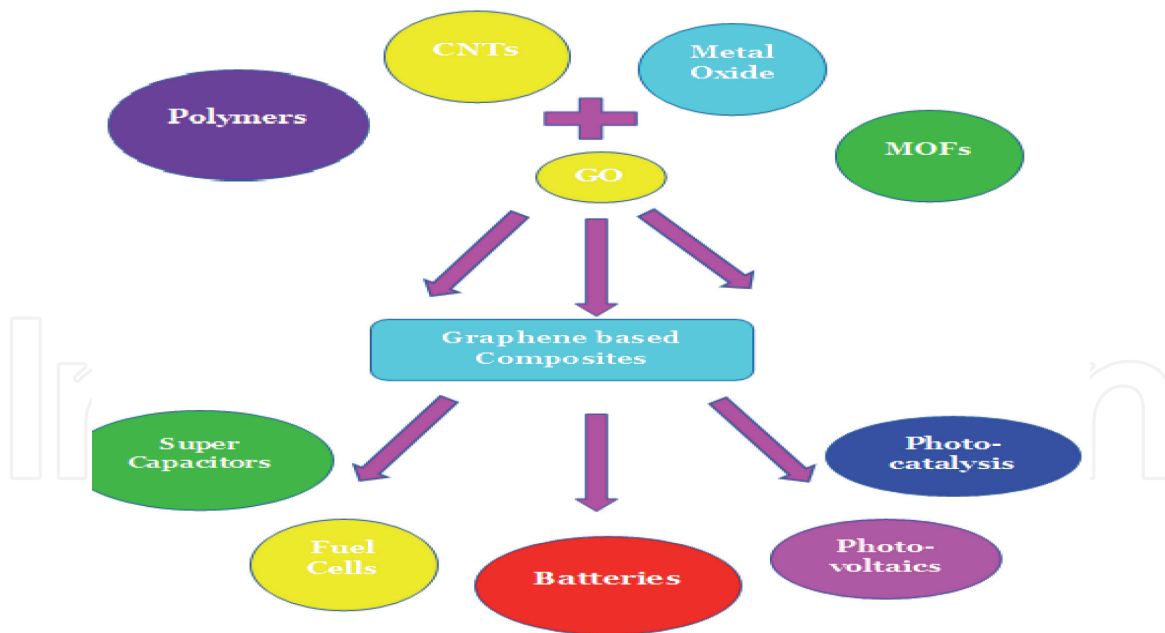


Figure 2.
Applications of graphene-based composite.

1.3.3 Graphene nanocomposites

Graphene nanocomposites are emerging as a class of exciting materials that hold promise for many applications. Generally, graphene-based composites are formed by incorporating polymer, ceramics or metal nanoparticles into graphene. The incorporation of such materials into graphene is very desirable for tuning the morphology of surface, electronic structure, and fundamental properties of graphene. The enhanced properties of the GO-based composites are because of excellent physical and chemical properties of GO and incorporated nanoparticles [26].

The functional groups of GO such as the epoxide, hydroxyl, carbonyl and carboxyl group offer the attaching points for nanoparticles. The larger surface areas and the conductive graphene structure facilitate the charge transfer and redox reaction and enforce the mechanical strengths of composites. Although graphene sheets naturally stack into multilayers and hence their high surface area and essential physical and chemical properties are lost, however, when nanoparticles are incorporated into it, graphene sheets can assist as support materials to anchor them and improve the properties of GO [24].

GO-based nanocomposites are the research hotspots nowadays due to their large-scale production and synergistically enhanced effect. Considerable efforts have recently been reported for decorating graphene with metal oxide nanoparticles. To date, several kinds of metal oxides such as TiO_2 , ZnO , SnO_2 , MnO_2 , Co_3O_4 , Fe_3O_3 , Fe_2O_3 , NiO and Cu_2O have been incorporated into GO [16, 27]. Nanoparticle growth on graphene sheets is a significant approach to produce nanocomposites or nanohybrids, as controlled nucleation and growth offer optimal chemical interactions and bonding between graphene sheets and nanoparticles, leading to very strong electrical and mechanical coupling within the nanocomposite. GO-metal oxide nanocomposites have been found as promising materials for lithium batteries, sensors, solar cells, fuel cells, photocatalysis and organic synthesis [16, 17, 24].

Recently, graphene and graphene-based nanocomposite have been extensively explored in emerging 3G solar cells particularly in DSSCs and PSCs. Graphene and its derivatives have been widely used as transparent conducting electrodes, electron donor or acceptor materials and counter electrodes, playing a substantial

role in increasing charge transport, reducing charge recombination and thus enhancing the performance of solar cell.

2. Graphene application in solar cells

2.1 Graphene application in DSSCs

A dye-sensitized solar cell (DSSC or DYSC) is a low-cost solar cell, invented by Swiss scientists Michael Grätzel and Dr. Brian O'Regan in 1991, and is often called as Grätzel cell (G Cell) [3]. DSSCs have attracted significant attention in search of substitute for silicon and thin-film solar cells due to their environmental friendliness, low fabrication costs and simple preparation process and remarkable conversion of solar energy into electricity [28]. DSSC is a photoelectrochemical system consisting of (a) transparent conducting working electrode (photoanode), (b) a dye sensitizer, (c) a counter electrode (cathode) and (d) an electrolyte [28, 29]. Its principle of operation is likened to natural photosynthesis process in plants. A monolayer of dye sensitizer absorbs incident light (like chlorophyll) giving rise to positive and negative carriers in the cell. On illumination, the electrons of the dye are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Then they are transported to the semiconductor's (TiO_2) conduction band (CB) and diffuse through the semiconductor, being collected at the transparent conducting oxide (TCO). An electrolyte solution which typically comprises of an iodide/triiodide (I^-/I_3^-) redox couple provides electrons to regenerate the oxidized dye. Eventually, the electrons transfer to the counter electrode (Pt) through the external circuit and reduces triiodide I_3^- ions back to the iodide I^- to complete the circle of conversion of photons into electricity (Figure 3) [12, 30, 31].

The photoanode is a key constituent, as it strongly influences the photovoltage (V), the fill factor (FF) and the incident photon-to-current conversion efficiency (IPCE) [12]. It serves as the main energy conversion center, converting photons into electrical energy, thus playing a critical role in DSSC [25]. A good photoelectrode is

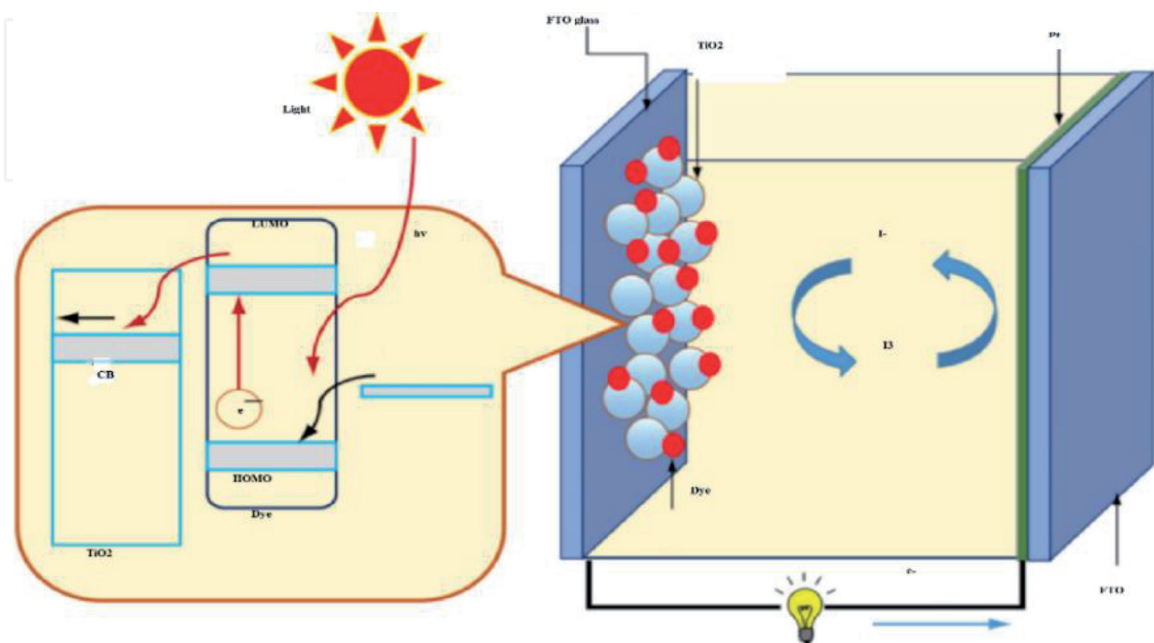


Figure 3.
Scheme diagram of dye-sensitized solar cells [12].

assumed to provide good usage of light, good electron injection and good electron collection. Various semiconducting (wide band gap) materials such as TiO₂, ZnO, SnO₂, CdS and Nb₂O₅ have been successfully used as photoanode in DSSCs [28, 32]. Among all, TiO₂ is most abundantly used, as it is nontoxic, cheap, chemically inert and easy to synthesize [33]. Moreover, TiO₂ have a wide band gap 3.2 eV; predominant chemical, electrical and optical properties; low recombination rate for the hole-electron pair; and great absorption property [12, 28]. The performance of DSSC is significantly influenced by properties like particle size, porosity and thickness of TiO₂ film.

Platinum (Pt) is the most widely used counter electrode (CE) in DSSC. Though Pt is very active to catalyze the reduction of triiodide, there are issues of stability in corrosive electrolytes and its high cost. Several efforts have been made to substitute it with less-expensive materials such as carbon materials and conducting polymers [34]. Carbon-based materials, such as graphite, carbon nanotubes, carbon black, nanocarbon and more recently graphene have been discovered severely as an alternative electrocatalyst for DSSC [17, 31].

Due to the exceptional mechanical, electrical and optical properties, graphene or highly reduced graphene are more appropriate as transparent electrodes, part of electrolyte, a light-harvesting dye and a counter electrode [17]. Additionally, work functions of graphene and rGO are calculated to be 4.4–4.5 eV, which are close to fluorine-doped tin oxide (FTO 4.4 eV) [25]. Thus, the tunable band gap of GO and its photon absorption ability in the visible and IR region permit to be a potential sensitizing material. The first application of graphene in DSSC as transparent conducting substrate was reported by Wang et al. [35] in 2008. They fabricated GO films by thermal reduction in Ar and/or H₂ flux from exfoliated graphite oxide. These films showed a transparency of more than 70% and a higher conductivity of 550 S/cm [35]. Subsequently, other roles of GO have been widely explored in DSSC.

2.1.1 G/metal nanocomposite as photoanode in DSSCs

Among the extensively used semiconductors, TiO₂ possess the longest diffusion length and lowest charge effective mass, but electron-hole recombination remains a significant issue [30]. Hence in order to reduce electron recombination and improve the stability of DSSC, graphene and graphene-based materials as photoanode have received great interest since the past few years.

The idea of using graphene into the photoanode of DSSC arises from the pioneering work of carbon nanotubes mixed with oxide nanostructures by Jang et al. [36]. This led to open an interesting field for researchers, quickly extended to graphene and its derivatives. The fascinating properties of graphene such as high transparency and Young's modulus make it a good candidate for transparent conducting substrates. The semimetallic properties and ultra-fast electron mobility allow graphene to serve as a charge carrier and as a transporter inside the semiconductor oxide layer in photoanode.

Kazmi et al. [31] used graphene-TiO₂ nanocomposites as photoanode for DSSCs. They synthesized Gr-TiO₂ with different graphene concentrations. Graphene nanoparticles were synthesized by modified Hummer's method, whereas TiO₂ nanoparticles were purchased from Sigma Aldrich. The band gap was found to be reduced from 3.16 eV to 2.2 eV with the increase in GO concentration. Furthermore, conductivity increases with graphene concentration which supports well with the reduction in band gap. PCE of DSSC was enhanced with the addition of graphene, and optimum results were found for 3.0 wt% of graphene concentration.

Nouri et al. [30] have reported nanocomposite photoanode titania photoanodes with reduced graphene oxide rGO for DSSCs. They carried out comparative study on two ex situ and one in situ doping of TiO₂ with rGO. The structural, optical and electrical characterization of the TiO₂/RGO nanocomposites and the PV performance of the DSSC were studied by several techniques. UV-vis spectroscopy showed that the existence of rGO resulted in narrowing of band gap and visible light absorption, particularly in solvothermal in situ TiO₂/RGO, representing chemical bonding between graphene sheets and TiO₂ nanoparticles. This chemical bonding has been verified by XPS and Raman spectroscopy. In situ doping of TiO₂ with RGO had the greatest beneficial effects on the performance of DSSC devices, yielding the highest Voc, Jsc, η and IPCE values. This was primarily ascribed to the role of RGO into the TiO₂ films to facilitate electron transport and decrease electron-hole recombination.

Kanta et al. [10] carried out comparative study of the promoting effects of graphene in TiO₂ photoanodes. They investigated the effect of the types and concentration of rGO on structural and photovoltaic properties of TiO₂-based electrodes. GO was synthesized by modified Hummer's method. The synthesis of rGO was carried out by using two different methods: chemical reduction with vitamin C and thermal reduction. The thermal reduction method was conducted in situ during the fabrication and heat treatment processes of the DSSCs. It was observed that DSSCs containing GO/TiO₂ photoanode (rGO by in situ thermal reduction) showed greater photovoltaic performance than rGO/TiO₂. It was also found that the PCE of the DSSCs changed with the concentration of graphene in a nonlinear manner. The 0.01 wt% GO/TiO₂ showed highest PCE (3.69%) values whereas for rGO based DSSCs 0.03 wt% rGO/TiO₂ showed maximum PCE (2.90%).

Xu et al. [22] synthesized TiO₂-RGO nanocomposites via an ultrasonication-assisted reduction method using GO in the TiO₂ precursor solution. The reduction of GO and the formation of TiO₂ crystals were carried out simultaneously. TiO₂-RGO was characterized by SEM-EDX, FTIR, XRD, Raman, XPS, UV-vis and electrochemical impedance spectroscopy. By the introduction of RGO, absorption of light of octahedral TiO₂ was markedly improved. In the meantime, the PCE of DSSC containing TiO₂-RGO photoanode was also found to be highly improved.

Jamil et al. [28] fabricated DSSCs using G-Nb₂O₅ photoanode. Nb₂O₅ due to higher conduction band edge and open-circuit voltage is attracting attention. In order to reduce charge recombination and improve charge collection efficiency, an electrically conductive carbon material such as graphene was carried out. The performance of material and DSSC was characterized using X-ray diffraction, SEM, FTIR, diffuse reflectance UV-Vis spectroscopy and potentiostat. Studies showed that the incorporation of graphene enhanced the absorption and decreased the band gap resulting in an increase in the electrical conductivity and decrease in charge recombination rate. Moreover, IV measurements of the G-Nb₂O₅ cells showed the 68% increase in fill factor and 52% increase in efficiency (PCE) as compared to cells using Nb₂O₅ nanoparticles as a photoanode.

Effendi et al. [37] fabricated a Gr-ZnO nanocomposite photoanode for DSSCs by electrodeposition process. The DSSCs based on Gr-ZnO nanocomposite were studied through electrochemical impedance spectroscopy (EIS), UV-Visible diffused reflectance spectroscopy (UV-Vis) and photovoltaic performances J-V curves. EIS showed that a lesser charge transport time constant arisen in DSSCs based on Gr-ZnO nanocomposite as compared to ZnO. This enhanced the electron collection efficiency, resulting in high open-circuit voltage. Moreover, Gr-ZnO nanocomposite

showed an effective photo-induced charge separation and transportation, thus exhibiting maximum photocurrent response as compared to ZnO. Moreover, The J-V curves demonstrated that incorporating graphene into the ZnO photoanode can permit the DSSC devices operate more efficiently. Gr-ZnO nanocomposite showed a maximum power conversion efficiency of 7.01%, which is doubled from pure ZnO photoanode.

Chou et al. [32] fabricated GO-TiO₂ and zinc oxide nanowires (ZNWs) as photoelectrode layer of DSSC. The morphology and effects of ZNWs/GO-TiO₂ were examined by the field emission scanning electron microscopy (FESEM), UV-visible spectrometer and solar simulator. The improvement of the photovoltaic performances of DSSC was due to the high specific surface area of GO and high electron mobility of ZnO. In addition, the electrochemical properties of GO-TiO₂/ZNWs double structure were studied by electrochemical impedance spectroscopy. The high surface area of GO and the high electron mobility of ZnO could enhance the photovoltaic performances of DSSCs. Compared with the different composite films, the ZNWs/GO-TiO₂ obviously showed higher dye loading. The optimal 3.82% PCE was achieved in DSSCs when the ZNWs/GO-TiO₂ composite film was modified with 1.5 mL GO solution, which was 70.09% more than TiO₂-based DSSC (3.82%).

Batmunkh et al. [38] used SnO₂ and reduced SnO₂-RGO as photoanode in DSSCs synthesized by microwave-assisted method. The incorporation of RGO into SnO₂ resulted in greater electron transfer, thus enhancing the PCE of device by 91.5%. The improvement in efficiency can be ascribed to increase loading of dye, addition of suitable energy levels and enhanced electron transport of the photoanode (Table 1).

Bykkam et al. [39] used few-layered graphene (FLG)/SnO₂ nanocomposite as a photoanode for DSSC. FLG varied from 1 to 3 wt %, and their effect was examined on the PCE. XRD patterns confirmed the existence of FLG and SnO₂ nanoparticles in FLG/SnO₂ nanocomposites. The band gap of SnO₂ nanoparticles was found to be ~4.239, 4.237, 4.210 and 4.172 eV for FLG (1.0, 2.0 and 3.0 wt%)/SnO₂ nanocomposites, respectively. An increased 3.02% PCE was observed for 1 wt% FLG/SnO₂ nanocomposite as compared to pure SnO₂ NPs. These results validated that suitable ratio of (1 wt%) FLG in SnO₂ achieves the role of blocking layer to decrease the back electron-hole recombination in DSSC and thus enhance the PCE, though the higher wt% of the FLG causes shielding of the FLG resulting in decrease of efficiency of DSSC.

Photoanode	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE %	Reference
TiO ₂	0.71	6.27	60.2	2.68	[10]
TiO ₂ -2%G			67.1	7.68	[31]
TiO ₂ -SnO ₂ -RGO(0.45)	0.67	10.185	46.1	3.16	[38]
FLG 1%-SnO ₂	0.54	12.21	45.6	3.02	[39]
G-ZnO/CdS	0.38	8.35	29	0.94	[26]
G-ZnO	0.91	10.89	66	7.01	[37]
G-Nb ₂ O ₅	0.196	0.363	42	0.11	[28]
Ti at 1% GO	0.68	8.42	63.9	3.69	[10]

Table 1.
 Photovoltaic parameters of various photoanode materials in DSSCs.

2.2 Graphene application in PSCs

The discovery of organo metal halide perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{halogen}$) as highly efficient light absorber in both photoelectrochemical and photovoltaic cells shed new light on emerging cheaper and highly efficient next-generation solution processed solar cells [7, 40]. Perovskite solar cells are a promising new substitute compared to silicon and dye-synthesized solar cells [2, 8]. PSCs have become the most promising photovoltaic technology, due to their high efficiency (certified 22.1%) and low cost in less than 8 years of development [4, 41, 42]. This extraordinary pace of development has gained much consideration and brought many engineers and scientists to this field.

Perovskite is named after the Russian scientist “Perovski” who first suggested the ABX_3 -type (e.g. CaTiO_3) crystal structure for perovskites. For solar cell applications, a new class of perovskite material, organo metal trihalide, has been recently introduced. In organo metal trihalide perovskites, “A” is an “organic monovalent cation” (e.g. CH_3NH_3^+), “B” is a “metal divalent cation” (e.g. Sn^{2+} or Pb^{2+}) and “X” is a “halide anion” (e.g. Cl^- , Br^- or I^-) [5, 41, 43].

Perovskite materials have exceptional properties such as a suitable band gap, high carrier mobility, broadband absorption of light, long carrier diffusion lengths and ambipolar transport due to which they have been explored as charge-transporting and light-absorbing materials in photovoltaic devices [41, 43]. A big advantage of PSCs is that they can react with light of various wavelengths, converting more sunlight into electricity and resulting in high efficiency. Furthermore, they are lightweight, flexible and semi-transparent. The first perovskite-based dye-sensitized solar cell $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{TiO}_2$ was developed in 2009 which obtained PCE of 3.13%, since then the PSCs have made an outstanding advancement, and in a period of 8 years, the PCE has been improved to around 23% (22.1% certified) [6, 44]. However, PSCs still face challenge of environmental and stability issues, which need to be improved.

Typically, PSCs with regular configuration (**Figure 4**) consists of three main layers:

- Electron transport layer (ETL)
- Perovskite absorber layer
- Hole-transport layer (HTL)

The foremost function of an ETL is the extraction of photo-generated electrons from perovskite and their transference to electrodes. ETL also acts as hole-blocking layer (HBL) [45]. The basic prerequisite for an ideal ETL is high conductivity, excellent electron mobility, high optical transmittance and an appropriate work function [8, 44, 46]. As far as PSCs are concerned, various ETLs such as TiO_2 , SnO_2 , Nb_2O_5 , ZnO , Zn_2SO_4 , In_2S_3 and BaSnO_3 have been used successfully using different techniques [46].

The HTL lies in the heart of solar cell in between the metal electrode and perovskite. It plays a vital role in the PSC structures and extracts positive charges (holes) from the perovskite and transports them to top electrode. It prevents the direct contact of Perovskite and top electrode [47]. The most widely used hole-transporting material is Spiro-OMeTAD. Other materials used as HTL are PEDOT:PSS, P3HT, PTAA, NiO, CuSCN, etc. [41, 47].

A PSC includes a perovskite (ABX_3)-structured compound as the light-harvesting active layer, most commonly organic–inorganic lead halide-based

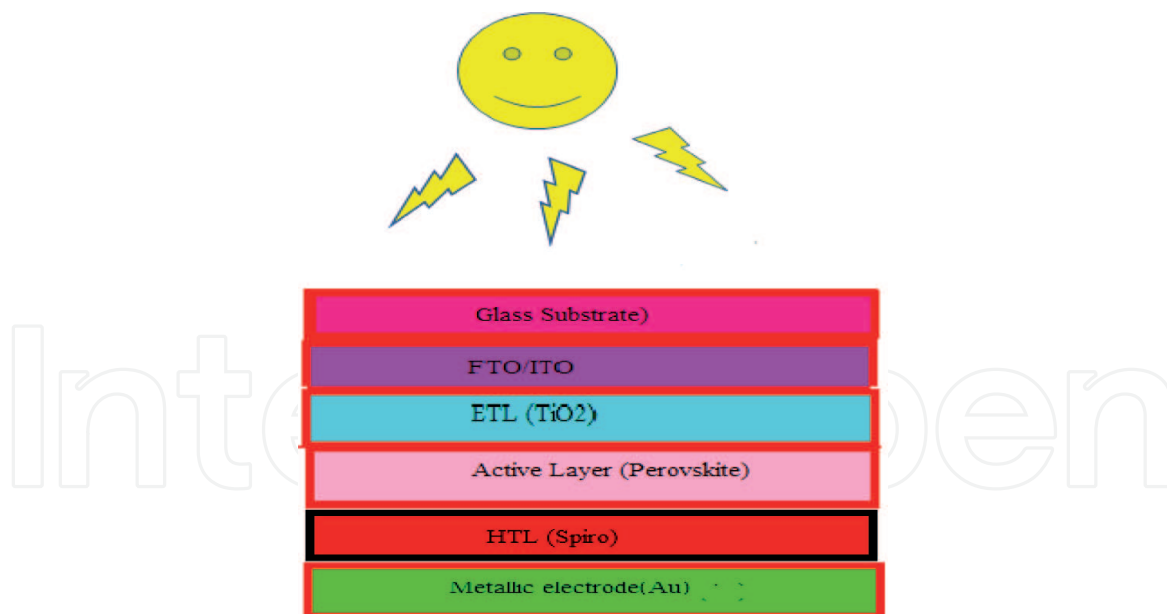


Figure 4.
Representative architecture of PSC.

material. The perovskites commonly used as active layer are methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and formamidinium lead triiodide ($\text{CH}_3(\text{NH}_2)_2\text{PbI}_3$) [4, 48]. Perovskite has a cubic crystal (**Figure 5**) structure with three-dimensional (3D) framework and shares BX_6 octahedron with the A ion placed at the octahedral interstices [4, 5, 47, 48]. The perovskite has unique ambipolar properties of generating and transporting both photo-generated holes and electrons. They act both as efficient light absorbers and charge carriers [47].

Theoretically, the working principle of photovoltaic devices involves four general processes as represented by **Figure 6**.

1. Absorption of light
2. Separation of charges
3. Transport of charge
4. Charge collection

Upon light illumination, the perovskite material undergoes photoexcitation and charge separation. The photoexcitation generates an electron-hole pair in the perovskite material. Then, diffusion of electrons and holes occurs toward the interfaces of perovskites/charge selective layers, respectively. After charge carrier (electrons and holes) extractions to charge selective layers, electrons and holes diffuse in the ETM and HTM, respectively, towards the corresponding electrodes for charge collection. These charge carriers produce a potential difference at the back and front contacts of the PSCs and can generate an electric current [4, 41].

In 2009, MAPbI_3 was first used as sensitizer by Miyasaka and coworkers in liquid-state DSSCs with a PCE of 3.81% [49]. In 2011, a PCE of 6.5% was reported for perovskite-sensitized DSSCs in which perovskite quantum dots were used as sensitizers [50]. However, a foremost advancement was achieved in 2012, using organometal halide perovskite sensitizers in perovskite-based solid state DSSCs (or PSCs), and PCEs of 9.7 and 10.9% were obtained [4]. Later, more exciting

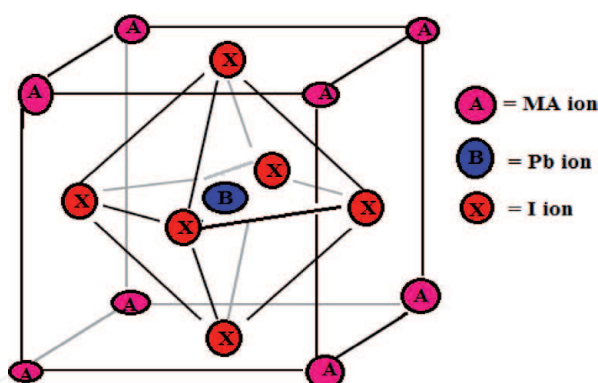


Figure 5.
Crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite.

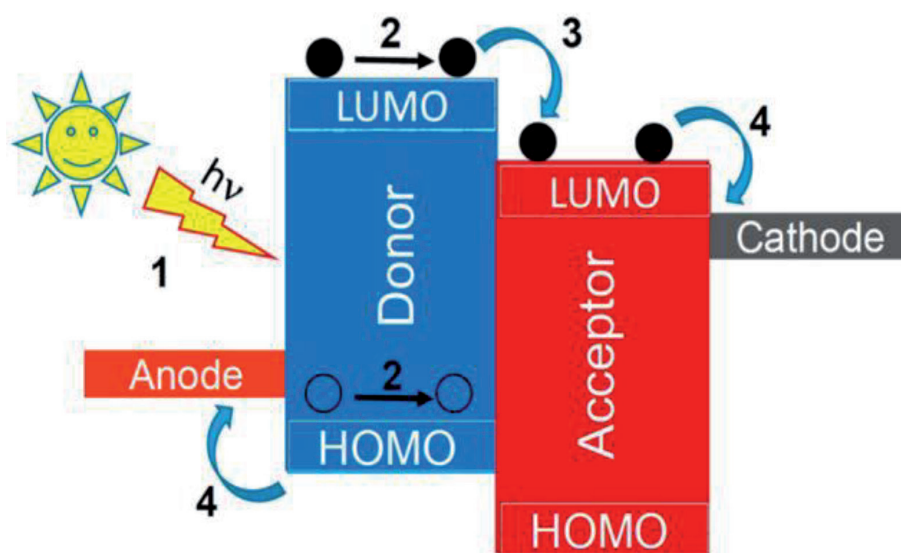


Figure 6.
Working principle of PSC [9].

discoveries and advancement on PSCs arose within a short period of time from 2012 to 2015, and a PCE of 22.1% was achieved [4].

2.2.1 Graphene/metal oxide as electron-transporting layer in PSCs

Though the highest efficiency in solution-processable PSCs have been achieved using metal oxide electron transporting layer, those electrodes require sintering at higher temperature of 500°C , which is not economical and unfavorable for the fabrication of PSCs on plastic substrates. Furthermore, the charge carrier recombination at a metal oxide/perovskite interface is another critical factor in PSCs that delays the charge transportation and decreases the PCE of a device. To report this problem, the graphene and its derivatives and graphene/metal oxide nanocomposites have been used as ETL [51]. Recently, some graphene/metal oxide nanocomposites such as G/ZnO, G/TiO₂, G/SnO₂, etc. have been used successfully as photoanode in PSCs.

Graphene nanocomposite with TiO₂ as a low-cost, low-temperature solution processed collection layer in mesostructured PSCs was fabricated by Wang et al. [52]. Graphene nanoflakes provided greater charge collection in nanocomposites, allowing the fabrication of devices at lower temperatures (150°C). These devices showed extraordinary photovoltaic performance with maximum PCE up to 15.6%. Hence, G/TiO₂ nanocomposites demonstrated its possibility to contribute significantly towards the progress of low-cost solar cells.

Han et al. [53], reported reduced graphene oxide/mesoporous (mp)-TiO₂ nanocomposite-based mesostructured PSCs that demonstrated an improved electron transport property due to the reduced interfacial resistance. The amount of rGO added to the TiO₂ nanoparticles was optimized, and their effects on electron diffusion, film resistivity, recombination time and photovoltaic performance were investigated. The rGO/mp-TiO₂ film decreases interfacial resistance when compared to the mp-TiO₂ film, and, thus, it improves charge collection efficiency. This effect significantly increases the VOC and ISC. The rGO/mp-TiO₂ nanocomposite film with an optimal rGO 0.4 vol% content showed 18% higher PCE than the PSCs using TiO₂ nanoparticles.

Saleem et al. [33] reported a new, low-temperature solution-processing approach to use rGO-TiO₂ composite material for the electron transport layer of PSCs. GO was synthesized by a modified Hummer's method and TiO₂ nanoparticles by hydrothermal method. Thin films of GO-TiO₂ were made with different wt.% of GO on indium tin oxide (ITO) substrate by spin coating, followed by annealing at 150°C. The band gap of the pure TiO₂ thin film was calculated to be 3.5 eV, which was reduced to 2.9 eV for the GO-TiO₂ nanocomposites with a red shift towards higher wavelength. Moreover, thermal post annealing at 400°C enhanced the transparency in the visible region and decreased the sheet resistance. The I-V study indicated an ohmic contact with the ITO substrate.

Chandrasekhar and Komarala [51] fabricated PSCs using a graphene/ZnO nanocomposite (G/ZnO NC) as an electron-transporting layer. ZnO and G/ZnO NC films were developed by a novel spray deposition method compatible with large-area processing methods for deposition of pristine. The effect of amount of graphene concentration was studied, and GO amount varied from 0 to 1 wt% in the G/ZnO NC films. It was found that a 0.75 wt% GO concentration in the G/ZnO NC films gives the best PSC performance with ISC and PCE going up from 15.54 to 19.97 mA cm⁻² and 7.01 to 10.34%, respectively, as compared to pristine ZnO. The improvement in PV performance is ascribed to the higher growth of the perovskite thin film and enhanced electron transport/extraction by using the graphene amount in the NC.

Xie et al. [54] improved the electronic properties of SnO₂ by adding minute amount of graphene quantum dots (GQDs) and reported improvement in electronic properties of SnO₂. The photo-generated electrons in GQDs can be easily

Electron-transporting layer	VOC (V)	J _{SC} (mA/Cm ²)	FF (%)	PCE (%)	Reference
TiO ₂ NP	1.0	17.7	61.0	10.1	[52]
High-temperature-sintered TiO ₂	1.00	21.4	70.0	14.1	[52]
SnO ₂	1.10	22.1	73.6	17.91	[54]
SnO ₂ -sintered free	0.91	20.73	64.2	12.10	[42]
SnO ₂ nanobelts	1.08	22.46	66.0	16.02	[46]
SnO ₂ /GQDs	1.134	23.05	77.8	20.31	[54]
G-SnO ₂	1.84	22.66	82.1	20.16	[55]
(0.4 vol %) rGO/mp-TiO ₂	0.91	21.0	70.8	13.5	[53]
TiO ₂ + graphene	1.04	21.9	73.1	15.6	[52]
0.75 wt% G/ZnO	0.926	19.97	56.3	10.34	[51]

Table 2.
Photovoltaic parameters of various electron-transporting materials in PSCs.

transferred to the conduction band of SnO₂, thus enhancing the conductivity of SnO₂ and reducing the charge recombination at the interface. SnO₂/GQDs fabricated solar cell showed low hysteresis and average PCE of 19.2%.

Xiaojuan et al. [55] tried to incorporate chemical modified (2D naphthalene diimide) graphene into SnO₂ nanocrystal as ETL for highly efficient PSCs. They modified SnO₂ with 2D naphthalene diimide-graphene, which can increase the surface hydrophobicity and is responsible for the van der Waals interactions between surfactant and perovskite. Thus, highly efficient PSCs were fabricated with maximum PCE of 20.2% and enhanced fill factor of 82%, which could be attributed to the improved electron extraction ability, electron mobility and the reduced carrier recombination, resulting in the increased FF. This work provides an important direction for further search in utilizing carbonaceous materials for low-temperature solution-processed planar PSCs (**Table 2**).

3. Conclusions

Graphene, due to its unique properties, has been explored widely in solar cells, and graphene metal oxide nanocomposites have been widely used in emerging third-generation solar cells. In view of reported literature, it is obvious that these materials played a significant role in enhancing the efficiency of 3G solar cells. In this chapter, the use of graphene nanocomposites has been explored in DSSCs and PSCs. Graphene nanocomposites as photoanode material in DSSCs seemed to be a promising approach to increase the charge transport, charge separation and thus the performance of solar cell. The low cost of graphene brings new prospects for commercialization, particularly to replace the use of Pt as counter electrode in DSSCs. In PSCs, the use of graphene and its derivatives with metal oxide (G/metal oxide nanocomposites) as electron transport layer has shown to be valuable. Incorporating of graphene into metal oxide reduces the series resistance and the charge recombination between perovskite and metal oxide as well as improves the electron and hole transport from the perovskite layer to the corresponding electrodes. Moreover, graphene nanocomposites have proved to be an efficient electron-transporting layer fabricated at lower temperature, thus suitable for flexible substrates in PSCs. Furthermore, these materials are interesting to replace Pt-FTO or ITO and noble metals (silver or gold) in 3G solar cells. Thus, the efficient replacement of the existing expensive materials reduces the cost of third-generation solar cells.

4. Futuristic aspects/prospective of graphene metal oxide nanocomposites

Graphene-based materials are interesting from the perspective of both fundamental science and technology due to their nontoxicity, chemical and thermal stability and mechanical strength. Although graphene metal oxide nanocomposites can be used to enhance the PCE of 3G solar cells by various optimization methods, manufacturing of highly efficient and stable solar cell is challenging. Moreover, much practical work needs to be done to obtain the optimal performance. From the future perspective, a mechanism for physical-chemical interactions of these nanocomposites in different layers of solar cells is necessary.

From energy point of view, graphene metal oxide nanocomposites can be used for energy storage and conversion devices such as solar cells, fuel cells, batteries, capacitors, etc. The unique graphene properties, such as high conductivity and

transparency, offer to replace the ITO, which lacks the flexibility and robustness in flexible solar cells, light-emitting diodes (LEDs), touch screens and displays. Graphene/metal oxide nanocomposites can be used to improve the durability of potential optoelectronic devices. Graphene/metal oxide nanocomposites are promising substitutes to decrease the drawbacks of using only metal oxide nanoparticles in various applications, such as anode materials in lithium ion batteries (LIBs), sensors, photocatalysts, removal of organic pollutants, etc. The graphene/metal oxide nanocomposites showed greater versatility as enhanced materials for the fabrication of electrochemical sensors and biosensors.

Graphene, due to its antibacterial, antiplatelet and anticancer activities, make it a potential candidate for biological and biomedical applications, and graphene/metal oxide nanocomposites can be used in cancer therapy, drug delivery, bioimaging, tissue engineering, etc. The synthesis, toxicity, biocompatibility and biomedical applications of graphene/metal oxide nanocomposites are important issues that require thorough investigation in any kind of applications related to human welfare.

Despite the substantial progress in the synthesis of graphene-based nanocomposites, challenges exist in the application on an industrial scale. For example, advanced applications of graphene/metal oxide nanocomposites require wide research to understand the interactions between graphene surface and the nanomaterials, which will have direct influence on the properties of these nanocomposites. An appropriate understanding of these interactions will surely enhance the application potential of the nanocomposites in various fields, such as catalysis, biosensing, drug delivery, imaging etc. Therefore, graphene metal oxide composites have vast potential for many industrial applications, and they are commercially feasible compared to carbonaceous-based nanocomposites.

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