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Chapter

# Materials for Photovoltaics: Overview, Generations, Recent Advancements and Future Prospects

*Muhammad Aamir Iqbal, Maria Malik, Wajeehah Shahid, Syed Zaheer Ud Din, Nadia Anwar, Mujtaba Ikram and Faryal Idrees*

## Abstract

As a consequence of rising concern about the impact of fossil fuel-based energy on global warming and climate change, photovoltaic cell technology has advanced significantly in recent years as a sustainable source of energy. To date, photovoltaic cells have been split into four generations, with the first two generations accounting for the majority of the current market. First generation of thin-film technologies is based on monocrystalline or polycrystalline silicon and gallium arsenide cells and includes well-known medium- or low-cost technologies with moderate yields, whereas, second generation includes devices with lower efficiency and manufacturing costs. Third generation is based on novel materials and has a wide range of design options, as well as expensive but highly efficient cells. However, fourth generation, also known as "inorganics-in-organics," combines the low cost and flexibility of polymer thin films with the durability of innovative inorganic nanostructures (metal nanoparticles or metal oxides) in organic-based nanomaterials (carbon nanotubes, graphene, and their derivatives). The aim of this chapter was to highlight the current state of photovoltaic cell technology in terms of manufacturing materials and efficiency by providing a comprehensive overview of the four generations as well as the relevance of graphene and its derivatives in solar cell applications.

**Keywords:** efficiency, generations, graphene, photovoltaics, polymers

## 1. Introduction

The rapid growth of the world's community and industrial area is leading to the great need for energy while renewable energy sources consumption such as geothermal, biomass, wind, and photovoltaic sources are challenging the planet's survival having its adverse effects. From the above-listed energy sources, photovoltaics is the technology used for the conversion of sunlight into electrical power by means of semiconductor materials. By considering their history, in 1883, Fritts worked on photovoltaics applications for the first time [1]. In 1954, the p-n junction diode potential was discovered at Bells laboratory with the efficiency of 6% using silicon material [2], and the same work has also been reported to make heterojunction solar cells based on $Cu_2S/CdS$ [3]. These diodes work on the phenomenon of generated voltages when sunlight falls on them. In the 1960s, the photovoltaic system for the first time was employed in commercial applications for space solar cells to deliver the power for satellite applications [4], and silicon semiconductor materials have been reported to be widely used in photovoltaic technology [5]. Moreover, in spite of the extensive use of silicon semiconductor-based technology, it has a high cost, which is the main drawback of not using this technology for home-based device applications. To overcome these challenging problems, researchers have put their efforts to replace silicon-based solar cells technology with the one having superior results [6]. Several researches show numerous classifications of materials, such as organic, inorganic, and hybrid materials, to potentially replace silicon materials from existing solar cells technology [7].

## 2. Overview of solar cell technology

Solar cells can be categorized according to their material composition whereas silicon-based semiconductors are dominant in the industrial share of photovoltaics, and despite considering the advantages of silicon material in photovoltaics, they lack some factors, such as very low absorbing power as well as needing almost 200–300 semiconducting material films to absorb the incident sunlight.

To overcome the lacking of silicon-based semiconductors, alternative technology was developed with solar cells having a micron-sized thickness, low cost but also low efficiencies [8], while thin sheet solar cells technology was also developed on flexible sheets. The advanced technologies are cadmium telluride, copper indium gallium selenide, and thin film-based technologies with reported efficiency of 20% [9, 10]. Some of the cadmium telluride-based solar cells companies have gained tremendous success at the commercial level with an efficiency of about 11% [11]. However, silicon-based single-junction and multi-junction solar cells have an extensive history of their commercial use including different active layers, such as microcrystalline silicon or hydrogenated amorphous silicon germanium with varying efficiencies from 8 to 12%, but their high cost and low efficiencies have limited the use of silicon material in solar cells and introduced the improved model.

Considering the mechanism of solar cells as shown in **Figure 1**, when sunlight falls on solar cell's surface, it reflects off from the surface. If the photon energy is lesser than materials bandgap energy then incident light is directly passed out from the semiconductor without being absorbed but if the photon energy is more than materials bandgap energy then the semiconductor material absorbs that energy and

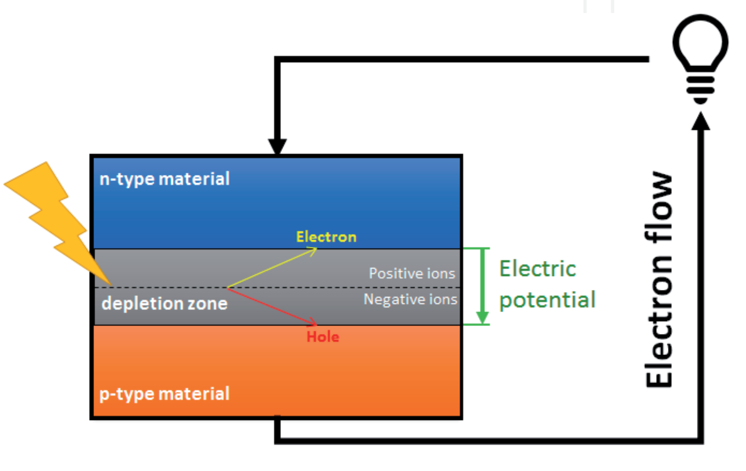


**Figure 1.**
*Schematic diagram of a solar cell [12].*

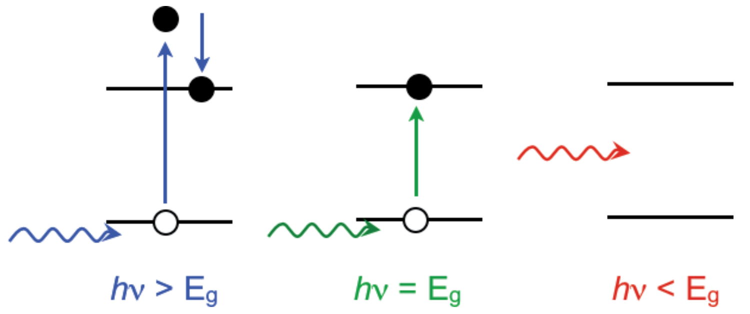


**Figure 2.**
*Photon energy compared to the bandgap energy of a semiconductor [13].*

excites electrons from valance to conduction band and generates electron-hole pair as shown in **Figure 2**. The advanced solar cells contain layers, such as the contact layer and window layer, which reduce the reflection losses by increasing the absorption efficiency of solar cells, resulting in electron-hole pairs that are then separated and driven to their collection electrodes. In p-n junction, the charge separation occurs by diffusion method and is collected by electrodes that generate current. However, the recombination process hurdles the carriers to reaching out to the electrodes, therefore not all the charge carriers got captured [13].

### 2.1 Approaches to light trapping

The solar cell surface is structured to trap the incident light within the semiconductor that enhances absorption over multiple passes while light trapping is the foremost mechanism of advanced solar cells. Silicon-based solar cells have a pyramidal surface structure that allows light to reflect from the cell surface to the silicon layer. The considerations for thick and thin-film light trapping designs are different—for thick films, light trapping can be defined using ray optics, although thin films can be treated with wave optics [13].

#### *2.1.1 Ergodic limit*

A thick film light trapping mechanism can be demonstrated with ergodic behavior if the cell texture is fair enough to randomize the light direction within a solar cell. The total internal reflection between the semiconductor material and surrounding medium generates the refractive index contrast which enhances photon path length within the semiconductor material, and hence absorption capacity. However, some portion of light may leave the semiconductor through an exit cone of some angle [13].

#### *2.1.2 Thin films*

In the case of smooth thin films, various mechanisms are used to exhibit absorption, such as interface reflection and refraction, material thickness, and light coherence. If the incident light coherency is greater than the film thickness, then it may act as a Fabry–Perot cavity, which serves as a resonant absorber [14]. The Fresnel coefficients are used to calculate reflection and refraction at normal incidence angle with tracked phasors over multi-passes.

## 3. Solar cell generations

Photovoltaic cells are categorized into four main classes according to their modifications, and these classifications are called generations [15]. **Figure 3** depicts materials that comprise each generation while **Figure 4** represents a historical overview of efficiencies of solar cells.

### 3.1 First-generation photovoltaic solar cells

The first-generation of photovoltaic solar cells is based on crystalline film technology, such as silicon and GaAs semiconductor materials. Silicon (Si) is the extensively used material for commercial purposes, and almost 90% of the photovoltaic solar cell industry is based on silicon-based materials [17], while GaAs is the oldest material that has been used for solar cells manufacturing owing to its higher efficiency. There are some advantages to use silicon material for photovoltaic solar cells manufacturing, such as:

- It is abundantly found in the earth's crust, which ensures its availability and could be inexpensive [18].
- It is a non-toxic chemical that delays the contamination process and durability loss that may occur when Si is used as a cell material.

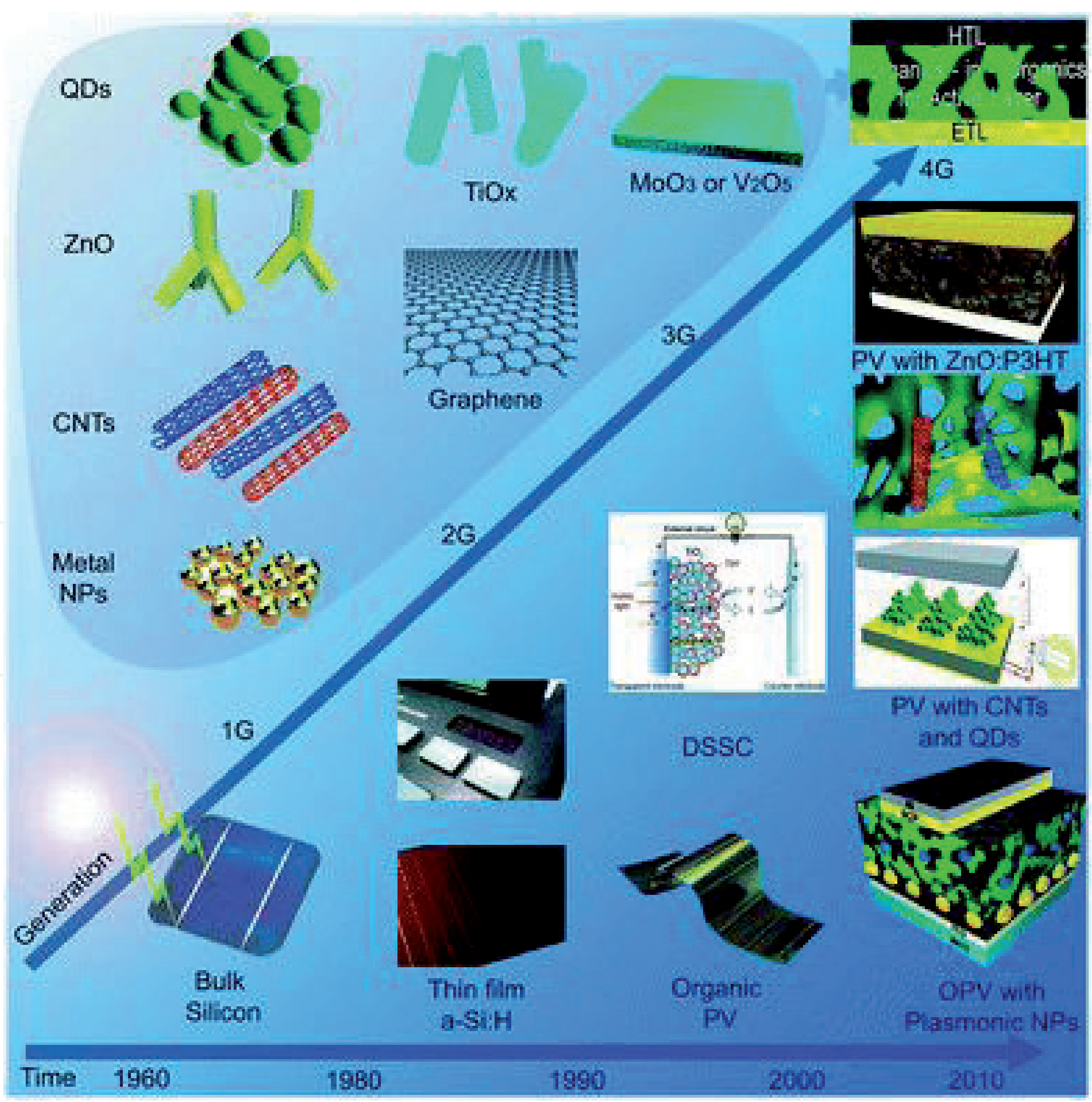


**Figure 3.**
*Four generations of photovoltaic cells along with the materials that comprise each generation [15].*

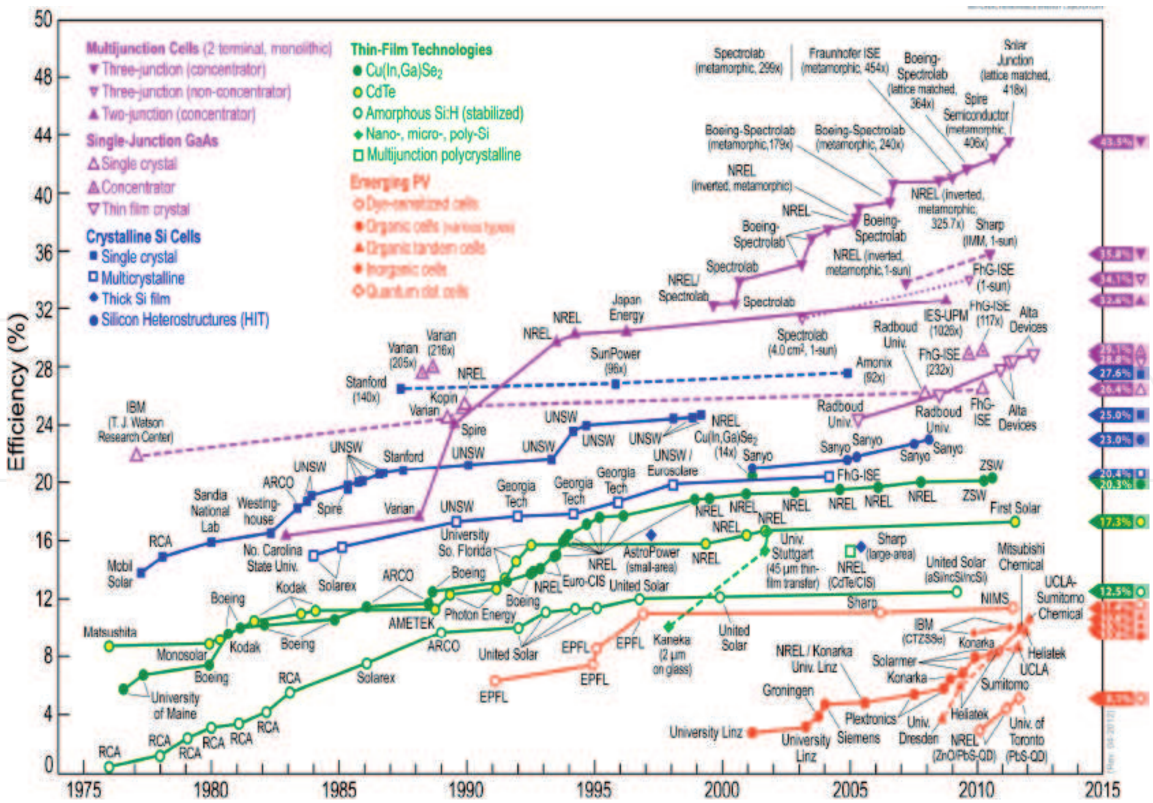


**Figure 4.**
*A historical overview of solar cell efficiency [16].*

- Silicon-based photovoltaic solar cells are easily compatible with the silicon-based microelectronic sector, resulting in the creation of the most interesting technologies [17].

The schematic representation of a silicon-based solar cell is shown in **Figure 5**. The GaAs has specialized use in multi-junction cells comprising several semiconductor materials and photovoltaic solar cells [19] having the following special characteristics:

- The GaAs has a bandgap of 1.43 eV that makes it an ideal material for single-junction photovoltaic solar cells.

- It has a good absorption power, so a few micron-thickness cells can produce a very strong absorption spectrum while silicon-based cells need a thick material to reach this limit of absorption.

- Because of the many doping chemicals that can modify the optoelectronic characteristics of a solar cell, GaAs can generate a multifunctional cell structure.

- Also, because of low-temperature coefficients, GaAs-based solar cells have the least influence on temperature.

Hence, the first-generation photovoltaic solar cells can be further classified into monocrystalline, polycrystalline, and GaAs solar cells.

### 3.2 Second-generation photovoltaic solar cells

The second-generation photovoltaic solar cells have the main focus of cost minimization that was the main issue of first-generation photovoltaic solar cells, and this can be achieved using thin-film technologies by reducing the material quantity as well as

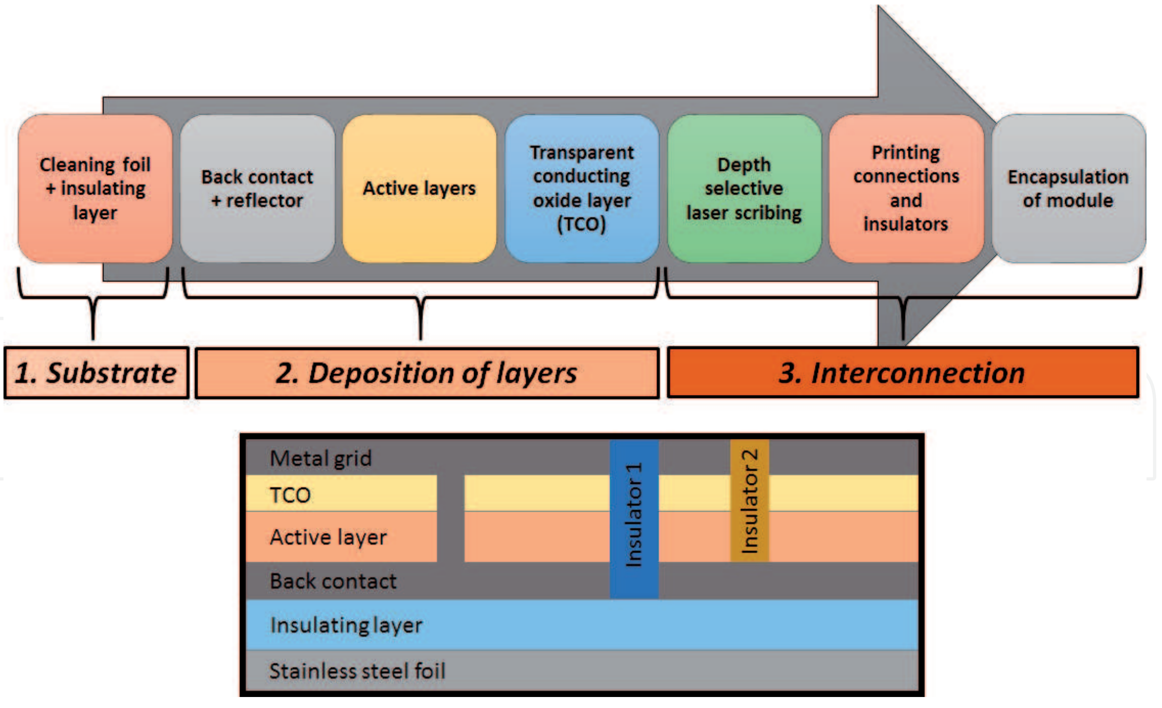


**Figure 5.**
*Schematic representation of a silicon-based solar cell [12].*

improving its quality. This modification is based on materials that showed good results in first-generation development and were extended to a-Si, c-Si, CdTe, and copper indium gallium selenide (CIGS) [15]. The advantageous factors of second-generation photovoltaics are listed below [20, 21];

- They are cheaper because of less material usage, up to a few microns in thickness.
- They have a maximum absorption coefficient.
- They can be used for vacuum and non-vacuum processes.
- This technological advancement can reduce the production steps by allowing direct integration to high-voltage modules.

However, some of the drawbacks are still present and listed below:

- Second-generation solar cells are less efficient as only 20% efficiency has been reported for CIGS [16].
- It has a fast degradation phenomenon through induced light, which limits its outdoor applications.
- The availability of raw materials may also be a limiting factor in some technologies.

### 3.3 Third-generation photovoltaic solar cells

Third-generation photovoltaics emerged from the gap left by second-generation technologies which required improved device efficiency via thin-layer deposition and intend to introduce novel materials with new techniques [22]. This sophisticated technology may be costly but the cost per watt peak would be decreased. As this technique is nontoxic and uses readily accessible materials, it is best suited for large-scale photovoltaic solar cell applications. These materials might be organic or nanostructured with high efficiency of more than 60% achieved by the use of different charge carrier collecting methods [23]. More emphasis has been placed on charge carrier mechanism, charge collecting, and energy capture improvements in third-generation photovoltaic solar cells. The important technologies used in third-generation photovoltaic solar cells are—dye-sensitized solar cells (DSSCs), organic and polymeric solar cells, perovskite cells, quantum dot cells, and multi-junction cells. The considerable advantages of third-generation photovoltaic solar cells may include solution-processable technologies, efficient technologies for commercial production, mechanical toughness, and high efficiencies at higher temperatures. However, the important challenge of this generation is to reduce the cost of solar electricity.

### 3.4 Fourth-generation photovoltaic solar cells

Fourth-generation photovoltaic solar cells combine the benefits of previous generations, such as lower cost, flexibility, and high stability of third-generation nanomaterials, metal oxides, graphene, and carbon nanotubes. These characteristics will give improved solar cell devices with the needed low-cost manufacturing as well as durability and the usage of nanomaterials in solar devices will aid to increase charge dissociation and transportation inside the cells. Because of its amazing properties and allotropic forms appearing in all four dimensions, graphene is a potential solar cell material with great scientific hopes in fourth-generation technological accomplishments [12].

## 4. Graphene and graphene-doped solar cells

Given the desire for renewable energy sources and their complete contributions to technological advancement, the demand for solar cells has increased with the added benefit of being low cost and simple to operate. Solar cells are not very efficient in general; it is the substance that makes them so. Recent developments in graphene-based solar cells boosted their efficiency about 20% by lowering the reflection of incident light. To improve the efficiency of solar cells, graphene may be doped in a variety of ways. Here is a thorough review of graphene-based solar cells and their doping variants that are being considered and researched across the world.

### 4.1 Principles of graphene-based solar cells

Graphene-based solar cells operate in the same way as conventional inorganic solar cells do today but the sole difference is that graphene or graphene-based materials replace inorganic components. Using graphene as a promising material in solar cells improves the adaptability along with tuneability of solar cells, while the number of graphene layers in a device and the doping effects are two essential characteristics that determine the efficiency of graphene-based devices. **Figure 6** depicts the schematic representation for inorganic and organic solar cells with graphene.

### 4.2 Graphene-silicon solar cells

Solar cells can also be implemented using carbon allotropes that are used for a wide range of applications and made them cost-effective. Some of the carbon allotropes show remarkable results while some are not much efficient because of the inability to tune their electronic properties and layer thickness. Graphene-based solar cells feature such efficient qualities, such as the capacity to modify layer thickness as per the requirement as well as the ability to tune properties based on the material combination. Graphene is used in solar cells with graphene-silicon combination with

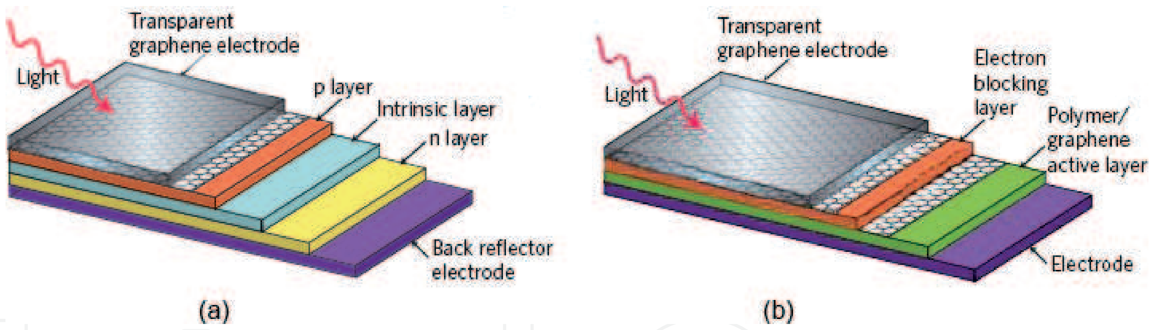


**Figure 6.**
*Schematic representation for (a) inorganic solar cells, and (b) organic solar cells with graphene [24].*

both p-type and n-type heterojunctions and as per reported literature, pure silicon solar cell's efficiency is better than any combination. However, graphene tuneability is much better in the case of hybrid solar cells and in the phase of advancement to improve its efficiency compared with pure silicon. According to available research, n-type heterojunctions create about 0.55 internal voltages for electron-hole pair separation while Schottky junctions generate 1.5% efficiency with a filler factor of 56%. As a result, depending on the dopant, efficiency can be increased and gold particles doped in graphene sheets showed a 40% increase in efficiency [25].

### 4.3 Graphene-polymer solar cells

Graphene-polymer-based solar cells are gaining popularity in the market and these polymer materials may be organic and beneficial due to their simple production method, low cost, and easy tuneability. Graphene has been used in possible applications of coating, layering, and temperature annealing in electrodes as a hybrid material with a combination of organic-inorganic materials. The Fermi level of graphene and semiconductor sheets is closer for charge injection applications and they have strong energy characteristics. Graphene can be combined with polymers to produce a hybrid material with a reported bandgap of 3.6 V that prevents cathode to electrode electron transport. Graphene layers with a thickness of 2 nm are claimed to provide the best outcomes in terms of improved electrical resistance and electron transmission [26].

### 4.4 Graphene-quantum dot solar cells

Carbon allotropes such as graphene and carbon nanotubes when coupled with quantum dots can produce efficient solar cells and the graphene-quantum dot combination has potential applicable uses. They are synthesized using an electrophoretic and chemical bath deposition method which produces a layered pattern of graphene and quantum dots that have 18 layers of both materials. This combination is said to have 16% efficiency while graphene-carbon nanotubes have 7% efficiency. The combination of graphene and quantum dots provides a superior framework as well as rapid electron transport between graphene and quantum dots while limiting charge recombination [27].

### 4.5 Graphene-tandem solar cells

Tandem solar cells consist of more than two subcells combined together called multi-junction solar cells. According to studies, a single solar cell is almost 40% efficient but tandem solar cells based on graphene oxides are up to 86% efficient owing to their greater subcell combination, and as a result tandem configuration can improve the energy conversion of solar cells [28].

### 4.6 Graphene-perovskite solar cells

Perovskite solar cells have an intriguing bandgap that results in remarkable absorption properties which eventually results in increased energy conversion efficiency of a solar cell and because of their standard structure, this type of solar cell can easily be tuned by changing the required material. These cells also feature a graphene layer which accounts for only 0.6 weight-percent of a cell and any other proportion reduces device efficiency. This cell arrangement is a little more complicated but it results in higher energy conversion efficiency when compared to non-graphene oxide layer solar cells. When graphene oxide materials are employed in this sort of solar cell and coupled with a light absorber they serve as a hole-conductor. Considering graphene oxide's other applications, it increases interface wettability on the surface of a perovskite solar cell and reduces the hole transporting layer contact angle. In addition, the C-C bonds of graphene sheets absorb the hole transport layer molecules which improve interfacial contacts of solar cells and results in better device performance [29].

### 4.7 Graphene-organic solar cells

Organic solar cells like inorganic ones play an important role in industrial applications and because of their endurance and low cost, organic devices are becoming more popular in technology. Major inorganic components in solar cells are being replaced by hybrid organic-inorganic components that exhibit superior physical and chemical characteristics as well as easy processability, easy availability, environmental friendliness, and most significantly, cost-effective synthesis and manufacturing. The major disadvantage of recent solar cells is their environmental impact; however organic components address this issue by offering stability against chemical deterioration, temperature, humidity, and other factors [30].

### 4.8 Graphene bulk-heterojunction solar cells

Graphene is a potential material used in various applications including electrodes, donor-acceptor layers as well as active layers because of its promising properties, such as conductivity, flexibility, and transparency, that make it an efficient material. Multi-junction solar cells also depend on graphene specificity such as its thickness, annealing temperature, doping concentration, and so on. Graphene heterojunctions employ graphene-based solar cells as well and they all rely on how graphene and its derivatives are mixed in these cells. Transparent electrodes, gallium arsenide (GaAs) solar cells, and photovoltaic layers are the primary components of graphene heterojunction solar cells [31].

## 5. Future prospects

The photovoltaic solar cell is a fascinating research area in both academic and industrial fields with advances and breakthroughs occurring on a regular basis. Solar cells [32] are often manufactured utilizing silicon and inorganic materials which have significant limits in current uses. The development of improved organic graphene-based and graphene derivative-based materials, as well as narrow bandgap polymers, is revolutionizing the market by demonstrating their potential and perfect characteristics necessary for solar cell device structure applications. There has been tremendous development in the improvement of graphene-based solar cells and more work has to be done in the future to achieve further growth in this industry. Because of their capacity to enhance different characteristics, graphene-based solar cells are customizable and adaptable to future limits in solar research. However, by enhancing existing solar cells and illuminating the characteristics of already employed non-graphene-based solar cells or developing a new variety of graphene photovoltaics, it is clear that graphene will play an important role in this intriguing analog [33].

## 6. Concluding remarks

An overview of photovoltaic solar cells is provided in this chapter, along with illustrations of four generations as well as prospective applications of graphene and graphene-based materials. Briefly, the first-generation thin-film technology was based on monocrystalline or polycrystalline silicon cells and gallium arsenide while the second generation includes devices with lower efficiency and lower manufacturing costs. The third generation has novel materials and a wide range of design options and expensive but highly efficient cells; however, the fourth generation, also known as "inorganics-in-organics," combines the low cost/flexibility of polymer thin films with the durability of innovative inorganic nanostructures in organic-based nanomaterials. Recent developments in graphene-based solar cells boosted their efficiency about 20% by lowering the reflection of incident light.

## Author details

Muhammad Aamir Iqbal[1*], Maria Malik[2], Wajeehah Shahid[3], Syed Zaheer Ud Din[4], Nadia Anwar[3,5], Mujtaba Ikram[6] and Faryal Idrees[7]

1 School of Materials Science and Engineering, Zhejiang University, Hangzhou, China

2 Centre of Excellence in Solid State Physics, University of the Punjab, Lahore, Pakistan

3 Department of Physics, The University of Lahore, Lahore, Pakistan

4 International School of Optoelectronic Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan, China

5 School of Materials Science and Engineering, Tsinghua University, Beijing, China

6 Institute of Chemical Engineering and Technology, University of the Punjab, Lahore, Pakistan

7 Department of Physics, University of the Punjab, Lahore, Pakistan

*Address all correspondence to: maamir@zju.edu.cn

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