Perovskite Solar Cells: Current Trends in Graphene-Based Materials for Transparent Conductive Electrodes, Active Layers, Charge Transport Layers, and Encapsulation Layers

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1. Introduction

Recent advancements in technology have inevitably led to a significant increase in the global energy demand, whose traditional energy sources, such as fossil fuels and nuclear energy, are failing to meet needs due to their nonrenewable nature and consequent depletion. Moreover, fossil fuels and nuclear energy are major sources of environmental pollution, which is responsible for unfavorable global warming and climate change. Hence, there has been considerable research interest in sustainable and renewable energy sources, particularly solar energy, due to its natural abundance and environmentally friendly nature.

In this regard, solar energy is most commonly converted into electricity by making use of the first-generation solar cells, i.e., crystalline silicon solar cells, that are now commercially available, with high power conversion efficiencies (PCEs) of above 26% and superior environmental stability. However, the large-scale production of silicon-based solar cells is restricted by their high production cost, complicated fabrication procedures, rigidity, and PCE, which is almost close to the theoretical limit of 29.4%. As a result, the second-generation solar cells, i.e., thin-film solar cells, such as amorphous silicon (a-Si) solar cells, copper indium gallium selenide (CIGS) solar cells, and cadmium telluride (CdTe) solar cells, and the third-generation solar cells, such as organic solar cells (OSCs), perovskite solar cells (PSCs), and dye-sensitized solar cells (DSSCs), have been developed by using simple and low-cost fabrication procedures. Among these, the third-generation solar cells have gained significant research attention due to an abundance of low-cost materials, solution processability, flexibility, lightweight, environmental friendliness, and ease of scaling-up. Interestingly, PSCs are a rising star owing to their recent breakthrough in PCE, which has shown a rapid increase from 3.8% in 2009 to 25.5% for the current state-of-the-art PSCs.

The superior performance of PSCs is mainly attributed to the exceptional properties of metal halide perovskites, including the large absorption coefficient, direct and tunable bandgap, low exciton binding energy at room temperature, ambipolar charge transport characteristics, high charge carrier mobility, slow recombination kinetics, and long electron–hole diffusion length. Thus, metal halide perovskites are emerging semiconductor materials described by the general formula of ABX₃, where A is a monovalent cation, such as methylammonium (CH₃NH₃⁺; MA), formamidinium (CH₃(NH₂)₂⁺; FA), caesium (Cs⁺), or rubidium (Rb⁺); B is a divalent metal cation, such as lead (Pb²⁺), tin (Sn²⁺), or germanium (Ge²⁺); and X is a halide anion, such as iodide (I⁻), bromide (Br⁻), or chloride (Cl⁻).
When organic cations, such as MA or FA, or their composite, are used as the A-site cations, the resulting metal halide perovskites are regarded as organic–inorganic hybrid perovskites, and when inorganic cations, such as Cs\(^+\) or Rb\(^+\), are used as the A-site cation species, the perovskites are referred to as all-inorganic perovskites.

A typical PSC comprises the electrodes (anode and cathode), charge transport layers (the hole transport layer [HTL] and electron transport layer [ETL]), and the perovskite active layer, arranged in the conventional (n-i-p) or inverted (p-i-n) configurations, with either the mesoscopic or planar structure, as shown in Figure 1.

The substrate and bottom electrode are usually transparent to permit the passage of incoming light to the perovskite active layer, in which photon absorption and photogeneration of carriers occur. Due to the low binding energy of perovskite materials (2–55 meV),\(^{[44]}\) the generated holes and electrons diffuse quickly toward the HTL and ETL, respectively, with minimum recombination, where they are collected and transported to the cathode and anode, which subsequently transport them to the external circuit, to power a given load. For better device performance, the charge transport layers should offer proper energy level alignment at the perovskite active layer–electrode interface\(^{[45,46]}\) to promote the selective extraction and efficient transportation of photogenerated charge carriers from the active layer to their respective electrodes, which inhibits electron and hole recombination, and leakage current. In addition, the charge transport layers should be moisture- or air-resistant and should have high thermal stability to protect the device from rapid degradation.\(^{[37,48]}\)

At their inception in 2009, PSCs were based on the solid-state DSSC principle and had the mesoscopic structure, containing MAPbX\(_3\) (X = I and Br) as the photosensitizer on an n-type mesoporous titanium dioxide (TiO\(_2\)) semiconducting layer in a lithium halide-based electrolyte, and exhibited a PCE of 3.8%.\(^{[33,34]}\) This was improved in 2012 by Kim et al.,\(^{[49]}\) who developed the first all-solid-state PSC through depositing MAPbI\(_3\) onto the mesoscopic TiO\(_2\) surface and used 2,2’7,7’-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobi fluorene (spiro-OMeTAD) as the solid HTL to replace the liquid electrolyte, resulting in a PCE of 9.7%. Besides enhancing the PCE, the all-solid-state PSCs helped to overcome the major problem of liquid perovskite-sensitized solar cells, originating from the inherent instability of the perovskite films upon exposure to the liquid electrolyte. Nonetheless, the mesoscopic layer usually requires high-temperature processing, which is incompatible with roll-to-roll fabrication on flexible substrates.\(^{[50,51]}\) As a consequence, recent studies are now focusing on p-i-n type planar PSCs, in which the traditional TiO\(_2\) mesoscopic layer is replaced by a simple TiO\(_2\) compact layer, due to the low-temperature fabrication procedures of planar PSCs, which are compatible with flexible devices.\(^{[52-55]}\)

Although the recent PCE of PSCs is approaching that of silicon-based solar cells, the upscaling of PSCs is still limited by their poor long-term operational stability, originating from the unstable perovskite materials and commonly used ETL and HTL materials, which lead to the photocatalytic degradation of perovskite films upon exposure to UV radiation, heat, moisture, or oxygen from the environment.\(^{[56-62]}\) In addition, ion diffusion from the metal counter electrode to the perovskite layer also impairs the device’s stability.\(^{[63]}\) Furthermore, PSCs face some charge loss issues, emanating from defects inside the perovskite, charge transport, and electrode films, and at the interfaces between adjacent films, which, in turn, lower the device efficiency.\(^{[34,37,42]}\) As a consequence, numerous approaches, such as interfacial engineering, substituting the organic charge transport layers with their inorganic counterparts, developing chemically stable perovskite active layers and encapsulating the perovskite films from the surrounding environment, have been proposed so as to overcome these limitations and, hence, improve the device efficiency and stability. Also, most of the

![Figure 1. Schematic diagram of a) n-i-p mesoscopic, b) n-i-p planar, c) p-i-n mesoscopic, and d) p-i-n planar PSCs.](image-url)
high-performance PSCs are based on expensive materials, such as spiro-OMeTAD, gold (Au), and silver (Ag).\[64,65\] Therefore, further research on the development of novel, low-cost, abundant, and environmentally friendly materials with facile fabrication procedures is envisaged to help PSCs compete with their silicon-based counterparts by enhancing not only their PCE, but also their long-term environmental stability and cost-effectiveness.

In this respect, carbon-based nanomaterials, such as carbon nanotubes (CNTs), nanofibers, fullerene (C\textsubscript{60} molecules), graphene, and graphdiyne,\[66-72\] have been extensively studied as low-cost alternatives to overcome the challenge of poor long-term stability, without compromising the high efficiency of PSCs, due to their superior stability and excellent optoelectronic properties. Among these, graphene, a 2D semiconductor sheet of sp\textsuperscript{2}-hybridized carbon atoms, arranged in a honeycomb lattice structure, is preferred to other carbon-based materials due to its large specific surface area (\(\approx 2.63 \times 10^4 \text{m}^2 \text{g}^{-1}\)),\[73\] high optical transparency (\(\approx 97.7\%\)),\[74\] high charge carrier mobility (\(2.0 \times 10^5 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}\)),\[75\] excellent electrical conductivity (\(1.5 \times 10^5 \text{S m}^{-1}\)),\[76\] high Young’s modulus (\(\approx 1.0 \text{TPa}\)),\[77\] and superior environmental stability.

Graphene has been prepared by several techniques, such as epitaxy, mechanical exfoliation, chemical vapor deposition (CVD), and oxidation–reduction.\[78-82\] Among these, the epitaxial growth of graphene on semiconducting substrates, such as silicon carbide, often results in good quality graphene with superior performance, suitable for direct application in photovoltaic devices.\[83\] However, the incompatibility with large-scale synthesis and greater energy consumption of epitaxy often limit its choice. Also, mechanical exfoliation, which involves the peeling off of graphene sheets from graphite with Scotch tape, produces good quality graphene with few defects and excellent performance.\[84\] Nonetheless, it has drawbacks due to its low production rate, which makes it difficult to achieve large-scale production. On the other hand, CVD involves the high-temperature decomposition of carbon sources, e.g., ethylene and methane, on transition metal substrates, such as Cu and Ni.\[85\] Although CVD has the potential to produce high-quality graphene sheets with large surface area, it has some issues, such as the requirement for expensive vacuum equipment, high-temperature processing conditions, and the complexity of transferring the resulting graphene films from the original substrate to the target substrate, which can easily damage the graphene lattice.\[86,87\]

However, the chemical inertness of pristine graphene makes it insoluble in organic solvents, and it is not compatible with solution synthesis.\[89\] Consequently, derivatives of graphene, such as graphene oxide (GO) and reduced GO (rGO), have also been extensively studied owing to their merit of high solubility in organic solvents, which makes them compatible with low cost, simple, and large-scale solution-processing, thereby helping to overcome the main drawback of solution processing that emanates from the insolubility of pristine graphene. Thus, recent work focuses on the low-cost and simple oxidation-reduction method, which involves the oxidation of graphite carbon atoms, to introduce some oxygen functional groups, such as epoxy, hydroxyl, carboxyl, and carbonyl, into the graphite layers.\[88\] This increases the interlayer spacing for easier separation of the oxidized graphite layers to form GO sheets, which are then reduced by thermal or chemical treatment to form rGO. However, the covalent nature of the C–O bonds disrupts the sp\textsuperscript{2} conjugation of the hexagonal graphene lattice, which lowers electron mobility, thus making GO an insulator.\[89,90\] Interestingly, thermal or chemical reduction of GO to remove the oxygen functional groups facilitates the restoration of electron delocalization, which improves charge carrier transport and, hence, converts the insulating GO into electrically conducting rGO sheets.\[26,91\] Nonetheless, when compared with graphene, the partial restoration of electron delocalization renders rGO with relatively low electrical conductivity and optical transmittance; hence, further optimization of the optoelectronic properties of rGO is required for them to be comparable with those of pristine graphene.\[92\]

Most importantly, graphene-based materials have managed to reduce the defect density inside perovskite films, charge transport layers, electrodes, and at the interfaces between adjacent layers, as well as enhancing the optoelectronic properties and stability of the various device components.\[93\] Therefore, graphene-based materials have the potential to address the challenges limiting the commercialization of PSCs. To the best of our knowledge, relatively few studies have reported the recent progress on the application of graphene-based materials in PSCs, and of the few studies that have been done, most of them have focused on improving the PCE only, while neglecting the long-term stability, which should be considered for the commercial application of PSCs.

Hence, this review provides a comprehensive summary of the recent breakthroughs in PSCs, brought over the last 3 years (2018–2020), by the application of graphene-based materials as electrodes, charge transport layers, and additives to the perovskite active layers, with an emphasis on photovoltaic parameters, such as open-circuit voltage (\(V_{oc}\)), short-circuit current density (\(J_{sc}\)), fill factor (FF), and PCE, because they play a vital role in measuring the performance of PSCs, coupled with long-term operational stability. The PCE determines the performance of a solar cell and is given by the ratio of the power output (\(P_{out}\)), i.e., \(J_{sc} \times V_{oc} \times FF\), to the power input (\(P_{in}\)), where \(J_{sc}\) is the maximum current flowing through the cell when the electrodes are short-circuited, \(V_{oc}\) is the maximum voltage measured across the cell when no current flows, and FF is a measure of the PSC’s quality as a power source.\[9\] The merits, drawbacks, and future directions for the fabrication and commercialization of more efficient and sustainable PSCs are also discussed.

2. Electrodes

A typical PSC has two types of electrodes, namely, a transparent conductive electrode (bottom electrode) and a counter electrode (top electrode), as discussed in Section 2.1 and 2.2, respectively.

2.1. Transparent Conductive Electrode

The transparent conductive electrode should have a high optical transmittance in the visible region for more light to enter into the cell and high electrical conductivity for the efficient transportation of photogenerated current to the external circuit. In this respect, the high electrical conductivity and high optical
transmittance in the visible region of indium tin oxide (ITO) have led to its wide use as a transparent conductive electrode in PSCs. However, the high cost, scarcity and toxic nature of indium, limits the choice of ITO.\[94-97\] In addition, ITO is rigid and fragile; hence, it is incompatible with flexible substrates.\[98\] Also, ITO is vulnerable to ion diffusion into the perovskite absorber layer, which degrades device performance and long-term operational stability, and high-quality ITO is prepared using complicated and expensive vacuum deposition approaches.\[99\] As a consequence, fluorine-doped tin oxide (FTO) has been proposed as a relatively low-cost alternative transparent conductive electrode due to its high optical transparency in the visible range and high electrical conductivity. Nonetheless, the rough surface of FTO raises issues, such as short circuits and leakage current, which reduce device efficiency.\[100\]

Recently, novel materials, such as conductive polymers,\[101,102\] graphene,\[103-106\] CNTs,\[107,108\] transparent conductive oxides,\[109\] and metal nanowires,\[110-112\] have emerged as promising replacements for the traditional ITO and FTO transparent conductive electrodes, due to their high optical transmittance in the visible range and competitive electrical conductivity. Among these materials, graphene and its derivatives have attracted enormous research interest due to their low cost, nontoxicity, easy availability, superior stability, greater mechanical flexibility, and large specific surface area.\[73,77,113\]

Being motivated by this, Liu et al.\[114\] used hydrazine hydrate vapor to reduce GO, resulting in rGO films with an average optical transmittance of \(\approx 75\%\) in the visible region and a sheet resistance of \(3.4 \text{k}\Omega \text{sq}^{-1}\), and used them as transparent conductive electrodes in MAPbI\(_3\) active layer-based planar n-i-p PSCs, as shown in Figure 2a. This resulted in devices with a low PCE of 3.38%, which was attributed to the relatively high sheet resistance and low optical transparency of the rGO electrodes as compared with the conventional ITO and pristine graphene electrodes. Hence, future research on improving the electrical conductivity of graphene-based materials, while maintaining high optical transmittance in the visible region, is envisaged to significantly contribute toward the replacement of traditional ITO electrodes.

This was improved by Kim et al.,\[115\] Tran et al.,\[116\] and Jung et al.\[117\] who prepared graphene films by means of CVD and used them as transparent conductive electrodes in p-i-n, p-i-n, and n-i-p MAPbI\(_3\) active layer-based planar PSCs, respectively. The graphene-based electrodes exhibited high average optical transmittances of above 90% in the visible region and low sheet resistances of \(\approx 468, 81, \text{and} 261 \text{\Omega} \text{sq}^{-1}\), respectively. This subsequently resulted in corresponding devices with PCEs of 13.94%, 14.18%, and 14.42%, which were relatively lower than those of the ITO reference devices, due to the relatively high sheet resistance of graphene when compared with ITO. Nonetheless, the graphene-based PSCs could be flexed without cracking and managed to retain \(\approx 90\%\),\[115\] \(>90\%\),\[116\] and \(\approx 84\%\) of their original PCE after 1000 bending cycles at a bending radius of 2 mm, demonstrating their superior mechanical flexibility to the ITO-based devices that developed some cracks, under the same conditions. The typical normalized PCEs of graphene and ITO-based PSCs at a bending radius of 4 mm\[115\] are shown in Figure 2b. Furthermore, unlike the ITO-based PSCs, which showed a rapid drop in PCE, the graphene-based devices managed to retain above 90%,\[115\] 85%,\[116\] and 80%\[116\] of their initial PCE after storage for 250, 500, and 500 h, respectively, demonstrating their excellent long-term operational stability. Thus, the chemical inertness of graphene can facilitate its future application not only as a transparent conductive electrode, but also as a water- or air-resistant layer. Therefore, as a future research direction, it would be crucial to improve the PCE of graphene-based devices, without compromising their stability, e.g., by tuning the optoelectronic properties of the graphene-based electrodes.

In another study, Heo et al.\[118\] used bis(trifluoromethanesulfonyl)amide (TFSA)-doped graphene as transparent conductive electrodes in p-i-n-type FAPbI\(_3-x\)Br\(_x\) planar PSCs, which exhibited a higher PCE of 18.9%, when compared with 13.8% for the pristine-graphene-based devices, mainly due to the high visible region optical transmittance and good electrical conductivity of the TFSA-graphene electrodes. Also, the TFSA-graphene-based PSCs retained \(\approx95\%\) of their original PCE after storage for 1000 h under environmental conditions, without encapsulation, demonstrating their long-term stability. Furthermore, the TFSA-graphene-based devices were very flexible, as revealed by their ability to maintain \(\approx 35\%, 75\%, \text{and} 85\%\) of their initial PCE after 5000 bending cycles, at a bending radius of 4, 8, and 12 mm, respectively.
Shin et al.\cite{119} obtained a PCE of 17.15\% in their p-i-n-type MAPbI$_2$-based planar PSCs that utilized graphene co-doped with TFSA and Au nanoparticles (NPs) as transparent conductive electrodes. This outperformed the devices based on pristine graphene, TFSA-graphene, and Au NPs-graphene electrodes, which exhibited PCEs of 11.09\%, 15.67\%, and 15.83\%, respectively, demonstrating the significance of doping in improving the device efficiency. In a separate study, Shin et al.\cite{120} fabricated n-i-p-type MAPbI$_2$-based planar PSCs with 3-aminopropyl triethoxysilane (APTES)-doped graphene transparent conductive electrodes. The treatment of graphene with APTES led to a significant decrease in sheet resistance from $\approx$700 to 486 $\Omega$ sq$^{-1}$. This subsequently facilitated the efficient transportation of charge carriers, which suppressed electron–hole recombination and increased the $J_{sc}$, and, hence, improved the PCE from 12.82\% for the pristine graphene-based PSCs to 16.41\% for the APTES-graphene-based devices. Furthermore, the APTES-graphene PSCs demonstrated superior mechanical stability, as revealed by their ability to retain $\approx$80\% of the initial PCE after 3000 bending cycles, at a bending radius of 4 mm.

In a similar study, but with ethylene glycol (EG)-functionalized graphene as the transparent conductive electrode, Xu et al.\cite{121} fabricated n-i-p-type MAPbI$_2$-based planar PSCs with a PCE of 12.61\%, which was higher than 5.61\% for the pristine graphene-based devices. The improvement in device performance was attributed to EG functionalization, which enhanced the visible optical transmittance and lowered the sheet resistance of the bottom electrodes. This, in turn, allowed more light to reach the perovskite absorber for more photocurrent generation and facilitated the efficient flow of the generated carriers with minimum recombination, thereby increasing the $J_{sc}$, as shown in Figure 3a. Furthermore, the PSCs based on EG-graphene and as-prepared graphene, respectively, managed to retain $\approx$92.2\% and 57.9\% of their original PCE after 1000 bending cycles at a bending radius of 9 mm, as shown in Figure 3b, demonstrating their mechanical robustness and potential in the fabrication of flexible devices. Also, the EG-graphene devices showed a relatively small drop of $\approx$25\% in PCE after storage for 400 h, in comparison with the pristine graphene-based PSCs, which dropped their PCE by $\approx$65\% under the same conditions, thereby revealing the importance of graphene functionalization in enhancing the long-term stability of devices.

Silver nanowires (AgNWs) have also gained considerable research attention as potential candidates for transparent conductive electrode fabrication due to their competitive optoelectronic properties.\cite{122} However, AgNW electrodes are easily oxidized, resulting in poor device performance and stability,\cite{123} thereby limiting their choice. This problem has been addressed recently by integrating the AgNWs with graphene owing to the excellent stability and optoelectronic properties of graphene. Moreover, the synergy between AgNWs and graphene significantly increases the optical transmittance of the composite electrode to values above those of pristine AgNWs and reduces the sheet resistance of the graphene-AgNW electrodes to values lower than those of the ITO reference electrodes, resulting in efficient charge transport and, hence, better optoelectronic properties.\cite{124-126} In addition, the introduction of graphene helps to overcome the poor corrosion resistance of pristine AgNWs, resulting in more stable graphene-AgNW composite electrodes.

Kim et al.\cite{124}, Zhou et al.\cite{125}, and Jin et al.\cite{126} also used graphene-AgNWs as composite transparent conductive electrodes in MAPbI$_2$-based planar PSCs, which displayed PCEs of 15.80\%, 15.31\%, and 9.73\%, respectively, that were relatively lower than those of the ITO reference devices, probably due to the higher optical transmittance of the ITO films. Interestingly, the graphene-AgNW-based PSCs managed to retain $\approx$94\% of their initial PCE after a harsh bending test at a radius of 2 mm,\cite{124} indicating their outstanding flexibility, as well as retaining $\approx$90\% and 88\% of the original PCE after storage in air for 45 and 60 days, respectively,\cite{125} demonstrating their excellent long-term stability. This was an improvement on a previous study by Chen et al.\cite{110} in which n-i-p-type MAPbI$_2$-based PSCs with rGO-AgNW composite electrodes displayed a relatively low PCE of 9.62\%, mainly due to the relatively high sheet resistance and low optical transmittance of rGO, when compared with graphene. However, the incorporation of rGO onto AgNWs enhanced the optical transmittance in the visible region and anticorrosive ability of the resulting robust composite transparent electrodes, thereby outperforming the efficiency and long-term stability of pristine AgNW-based devices. Hence, in future research, composites of graphene-based materials and

![Figure 3. a) J-V curves and b) normalized PCE at a bending radius of 9 mm, of graphene-based PSCs. Adapted with permission.\cite{123} Copyright 2020, American Chemical Society.](www.advancedsciencenews.com)
Table 1. Photovoltaic parameters of PSCs with graphene-based transparent conductive electrode materials.

| Transparent conductive electrode | V_{oc} [V] | J_{sc} [mA cm^{-2}] | FF | PCE [%] | References |
|----------------------------------|------------|----------------------|----|---------|------------|
| rGO                              | 1.03       | 9.69                 | 0.34 | 3.38    | [114]      |
| Graphene                         | 1.02       | 19.85                | 0.69 | 13.94   | [115]      |
| Graphene                         | 0.93       | 20.90                | 0.73 | 14.18   | [116]      |
| Graphene                         | 0.91       | 20.92                | 0.76 | 14.42   | [117]      |
| Graphene                         | 1.02       | 21.0                 | 0.65 | 13.80   | [118]      |
| TFSA graphene                    | 1.07       | 22.7                 | 0.78 | 18.90   | [118]      |
| TFSA/Au NPs graphene             | 1.08       | 20.55                | 0.77 | 17.15   | [119]      |
| TFSA graphene                    | 1.06       | 20.84                | 0.71 | 15.67   | [119]      |
| Au NPs graphene                  | 1.05       | 20.85                | 0.72 | 15.83   | [119]      |
| Graphene                         | 1.02       | 17.84                | 0.61 | 11.09   | [120]      |
| Graphene                         | 0.99       | 18.58                | 0.70 | 12.82   | [120]      |
| APTES graphene                   | 1.07       | 20.75                | 0.74 | 16.41   | [120]      |
| Graphene                         | 0.72       | 12.37                | 0.63 | 5.61    | [121]      |
| EG graphene                      | 0.93       | 18.83                | 0.72 | 12.61   | [121]      |
| Graphene AgNWs                   | 1.01       | 20.96                | 0.75 | 15.85   | [124]      |
| Graphene AgNWs                   | 1.06       | 21.79                | 0.66 | 15.31   | [125]      |
| Graphene AgNWs                   | 0.96       | 16.48                | 0.62 | 9.73    | [126]      |
| rGO AgNWs                        | 0.87       | 15.43                | 0.71 | 9.62    | [110]      |

AgNWs can be used as potential alternatives to conventional ITO transparent conductive electrodes to fabricate high-performance and sustainable PSCs.

A summary of the photovoltaic parameters of PSCs that made use of graphene-based transparent conductive electrodes, discussed in this review, is presented in Table 1. From Table 1, PSCs with TFSA-graphene transparent conductive electrodes exhibited the best PCE of 18.90%,[118] whereas the rGO-based PSCs displayed the lowest PCE of 3.38%, mainly due to the relatively high sheet resistance and low optical transparency of rGO, in comparison with graphene, hence limiting the choice of rGO. Interestingly, the introduction of graphene-based electrodes not only enhanced the device performance, but also improved the mechanical flexibility and long-term environmental stability of PSCs. Therefore, as a future research effort, it would be vital to use approaches, such as introducing suitable dopants or fabricating nanocomposites of graphene-based electrode materials. This helps to minimize the sheet resistance of electrodes, without compromising their optical transmittance, as well as increasing their stability, which subsequently improves the efficiency and sustainability of devices, hence paving the way for the future commercialization of graphene-based PSCs.

2.2. Counter Electrode

The counter electrode is commonly prepared by depositing a noble metal, such as Au or Ag, on top of the cell, which not only has high electrical conductivity and well-matched work function with the perovskite film and charge transport layers, but also reflects some of the incident light, thereby increasing photon harvesting in the perovskite active layer.[127,128] However, the top metal electrodes are usually deposited under high vacuum conditions, mostly by thermal evaporation, which is expensive and consumes more energy.[129,130] In addition, the Ag top electrodes can be easily oxidized by oxygen in the surrounding environment, and at high temperature, the metal ions can diffuse through the charge transport layers to the perovskite active layer, thereby degrading device performance and long-term stability.[131] Also, the halide ions can migrate from the perovskite material and react with the metal electrodes to form metal halides, which impair device efficiency and stability.[132-134] Furthermore, the low optical transparency of metal counter electrodes is not compatible with the fabrication of semitransparent PSCs. These challenges, coupled with the high cost of Ag and Au, limit the large-scale production of PSCs; hence, this has prompted the search for low-cost alternative counter electrodes, with comparable performance and superior stability.

In this respect, alternative counter electrodes, including Al, transparent conductive oxides, Cu, and carbon-based materials,[64,135,136] have been recently investigated. Among these, the low cost, simple fabrication procedures, high optical transmittance, competitive electrical conductivity, excellent stability, and well-matched work functions of carbonaceous materials, particularly graphene and its derivatives, have rendered them with ample potential to replace conventional metal counter electrodes in PSCs.[137,138]

In this regard, graphene has been used as a counter electrode in planar PSCs, which exhibited PCEs of 10.06%[139] and 18.65%[140] which were slightly lower than those for metal counter electrode reference devices. The slight deviation in efficiency between graphene and metal counter electrode-based devices was ascribed to the relatively high series resistance of graphene films when compared with the metal electrodes. Although graphene-based PSCs had relatively lower PCEs than those of the metal counter electrode control devices, they displayed excellent environmental and thermal stability, as revealed by their ability to retain above 90% of their original PCE after storage for 1000 h at 85 °C in air, without encapsulation, as compared with the Au-based device, in which the PCE rapidly dropped within 500 h, as shown in Figure 4a. This was mainly attributed to the hydrophobic nature of graphene, which effectively blocked the penetration of moisture into the cell, as well as the chemical inertness and robustness of graphene owing to the strong connection between carbon atoms through strong covalent bonds. The graphene-based PSCs also showed a negligible drop in PCE after assembling and repeatedly disassembling for more than 500 times, as shown in Figure 4b, indicating their superior mechanical stability. Hence, as a future research direction, tailoring the properties of graphene counter electrodes, to enhance their electrical conductivity, without compromising their high optical transmittance and stability, is envisaged to result in highly efficient and sustainable devices, well suited for commercial applications.

Recently, nitrogen-doped graphene (N-graphene)[141] and 3D potassium-ion preintercalated graphene[142] have been used as counter electrodes in HTL-free PSCs, due to their proper energy level alignment with the perovskite film, as shown in Figure 5a, and high electrical conductivity, which facilitated the effective extraction and transportation of the photogenerated charge...
carriers with minimum recombination. This subsequently increased the $V_{oc}$, $J_{sc}$, and FF, resulting in devices with PCEs of 10.32% and 7.81%, respectively, which outperformed the pristine graphene counter electrode-based devices, and was comparable to devices based on metal counter electrodes. TFSA graphene\textsuperscript{[31]} has also been used as a counter electrode in all-graphene electrode semitransparent n-i-p-type MAPbI$_3$-based PSCs, which exhibited a maximum PCE of 11.22% and retained above 70% of the initial PCE after 1000 bending cycles at an 8 mm bending radius, demonstrating their excellent flexibility. In another recent study, Tian et al.\textsuperscript{[143]} used graphene/CNT composites as counter electrodes in PSCs, as shown in Figure 5b, which exhibited a high PCE of 15.36% and maintained 86% of the original PCE after storage under environmental conditions, without encapsulation for 500 h. In comparison with PSCs based on pristine CNT and Ag counter electrodes, the excellent performance and air stability of the graphene/CNT-based devices were attributed to the relatively high electrical conductivity and efficient moisture blocking capabilities of the hybrid graphene/CNT film. This reveals that the application of graphene-based materials as counter electrodes in PSCs not only improves the device efficiency, but also enhances the long-term stability, which is a significant step toward commercialization.

The photovoltaic parameters of PSCs using graphene-based counter electrodes, discussed in this review, are summarized in Table 2. Among these, devices with pristine graphene and graphene/CNT composite counter electrodes exhibited the best PCEs of 18.65%\textsuperscript{[140]} and 15.36%\textsuperscript{[143]} respectively, which were comparable to the metal counter electrode reference devices. Most importantly, the graphene-based counter electrodes resulted in more stable PSCs when compared with their metal electrode counterparts. Therefore, with future research efforts, graphene-based materials could become the next counter electrode choice for high-performance and more stable PSCs.
3. Active Layer

The active layer of PSCs is commonly made up of metal halide perovskites, which not only act as light harvesters due to their broad and intense absorption spectral range, but also act as ambipolar charge transporters.94 Currently, PSCs based on hybrid organic–inorganic perovskites as an active light-absorbing layer are more efficient than their all-inorganic perovskite-based counterparts.131 Most importantly, the compatibility with low-temperature synthesis and easy solution processability of perovskite materials allow their low-cost and large-scale production on flexible substrates. Also, precise tuning of the halide content is a promising way to easily manipulate the bandgap of perovskites, which, in turn, allows the optimization of light absorption and, hence, improves photocurrent generation, thus subsequently increasing the device efficiency.34,42,145 However, the delicate MA or FA organic cations often cause the organic–inorganic hybrid perovskites to have poor stability under exposure to heat, UV radiation, moisture, and oxygen.146,147

Although the high stability of inorganic cations renders them with ample potential to address the instability issue observed in their organic counterparts, the small size of inorganic cations has a negative impact on the phase stability of all-inorganic perovskites,131 hence limiting their choice. In addition, Pb-based compounds have a detrimental effect on the humans and the environment, so there has been significant research investigation on Pb-free perovskites.142 Although alternatives, including tin (Sn)-based organic–inorganic perovskites, have been widely studied as Pb-free systems, they still display relatively lower device efficiency.148,149 On the other hand, poor crystallinity of perovskite materials often impairs the device performance owing to high defect density, which slows down the free charge carrier diffusion rate, thereby causing charge carrier recombination, short carrier lifetime, and voltage loss.150–152

Hence, to overcome the aforementioned drawbacks, several additives, including carbon-based materials,130,153,154 metal halides,156 polymers,157 and acids,158 have been incorporated recently into the perovskite film. Among these, carbon-based materials, particularly graphene and its derivatives, are potential additives to the perovskite active layer material due to their wide absorption spectral range, high charge carrier mobility, and excellent thermal, chemical, and mechanical stability, good crystallinity, and less impact on the environment.45,159

In this regard, GO160,161 and GO–Cl162 have been introduced into the MAPbI$_3$ active layer of PSCs, as shown in Figure 6a. This significantly improved the crystallinity, morphology, optical absorption, and charge extraction efficiency of the perovskite film, together with reducing charge carrier recombination. This, in turn, enhanced the $J_{sc}$ and $V_{oc}$, as shown in Figure 6b, which subsequently increased the PCE from 16.10%, 9.20%, and 12.81% for the pristine MAPbI$_3$ reference devices, to 17.59%, 14.28%, and 15.14%, respectively. Interestingly, the devices with GO-modified perovskite layers displayed excellent stability, as revealed by their ability to retain ~96% of the initial PCE after storage for 30 days under environmental conditions.161

In addition, rGO163 functionalized-rGO (f–rGO) and molybdenum disulfide quantum dots (MoS$_2$ QDs):f–rGO,164 and nickel(II) oxide (NiO):rGO165 have also been incorporated into the perovskite active layer, which enhanced the energy level alignment at the perovskite layer/charge transport layer interface, thereby reducing the energy barrier for the efficient extraction and transportation of charge carriers. This resulted in rGO/ MAPbI$_3$, f–rGO/MAPbI$_3$, MoS$_2$ QDs:f–rGO/MAPbI$_3$, and NiO–rGO/MAPbI$_3$–Cl$_x$-based PSCs with the PCEs of 16.50%, 19.34%, 20.12%, and 20.77%, respectively, which outperformed the pristine perovskite reference devices. More importantly, the f–rGO/MAPbI$_3$ and MoS$_2$ QDs:f–rGO/MAPbI$_3$-based devices managed to retain ~88.8% and 91.2% of the initial PCE, respectively, after an aging test of 1032 h, demonstrating their superior stability to the pristine MAPbI$_3$ control devices, which maintained ~76.4% of the original PCE under the same conditions164 as shown in Figure 7. Also, the NiO–rGO/MAPbI$_3$–Cl$_x$-based devices dropped less than 3% of their original PCE, after storage for 310 days in air, without encapsulation. Hence, this reveals the potential of GO and rGO for use in future research as additives to the perovskite active layer, to improve the device efficiency and stability.

Recently, graphene QDs (GQDs),166 graphite-nitrogen-doped GQDs (GN-GQDs),167 and graphene-copper indium sulfide (CuInS$_2$) QDs168 have been introduced into the MAPbI$_3$ active layer of PSCs. This improved the crystallinity, light absorption, charge extraction, electrical conductivity, morphology, and

![Figure 6](image-url) Figure 6. a) Schematic diagram of a GO-MAPbI$_3$ or GO–Cl:MAPbI$_3$-based PSC, and b) $J$–$V$ characteristics of GO-MAPbI$_3$- and pristine MAPbI$_3$-based PSCs. Adapted with permission.161 Copyright 2019, Elsevier.
The variation of normalized PCE of pristine MAPbI$_3$, MoS$_2$ QDs-, f-rGO/MAPbI$_3$, and MoS$_2$ QDs:f-rGO/MAPbI$_3$-based PSCs with storage time. Adapted with permission.© 2018, American Chemical Society.

stability of the perovskite films. Hence, the introduction of graphene-based materials into the perovskite film reduced the defect density, increased the photogeneration of electron–hole pairs and carrier mobility, and minimized charge carrier recombination and leakage current. This resulted in devices with PCEs of 19.7%, 19.8%, and 17.1%, respectively, which outperformed their pristine MAPbI$_3$ counterparts. However, relatively higher concentrations of graphene-based additives caused the aggregation of active layer particles, which, in turn, acted as recombination centers or charge carrier traps that lowered the device efficiency. More importantly, the graphene-based devices managed to retain above 80% of their original PCE after storage for 30 days, without encapsulation, indicating their excellent air stability. Therefore, this demonstrates the potential of graphene and its nanocomposites, as additives to the perovskite active layer material, to enhance device performance and stability.

Table 3 summarizes the photovoltaic parameters of PSCs using graphene-based materials as active layer additives.

Table 3. Photovoltaic parameters of PSCs using graphene-based materials as additives to the perovskite active layer.

| Active layer | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF | PCE [%] | References |
|--------------|-------------|-----------------|----|---------|------------|
| GO-MAPbI$_3$ | 1.07        | 23.73           | 0.69 | 17.59   | [160]      |
| GO-MAPbI$_3$ | 1.07        | 18.82           | 0.71 | 14.28   | [161]      |
| GO-Cl:MAPbI$_3$ | 1.03 | 24.56           | 0.69 | 15.14   | [162]      |
| rGO-MAPbI$_3$ | 1.00        | 22.90           | 0.72 | 16.50   | [163]      |
| f-rGO/MAPbI$_3$ | 1.07      | 22.49           | 0.81 | 19.34   | [164]      |
| MoS$_2$ QDs:f-rGO/MAPbI$_3$ | 1.11 | 22.81           | 0.80 | 20.12   | [164]      |
| NiO-rGO/MAPbI$_3$-Cl$_x$ | 1.05 | 25.89           | 0.72 | 20.77   | [165]      |
| GQDs-MAPbI$_3$ | 1.13        | 23.86           | 0.70 | 19.70   | [166]      |
| GN-GQDs/MAPbI$_3$ | 1.06 | 23.40           | 0.80 | 19.80   | [167]      |
| Graphene-MAPbI$_3$ | 0.96 | 12.50           | 0.62 | 7.40    | [168]      |
| Graphene-CuInS$_2$ QDs/MAPbI$_3$ | 1.05 | 21.40           | 0.76 | 17.10   | [168]      |

The charge transport layers help to reduce the energy barrier between the perovskite active layer and the electrodes for the effective extraction and transportation of photogenerated holes and electrons from the perovskite layer to their respective electrodes. Thus, charge transport layers help to enhance the electrical contact at the perovskite layer–electrode interface, which improves charge extraction, transportation, and collection efficiency. The charge transport layers selectively allow the transportation of a specific type of charge, i.e., holes for the HTL and electrons for the ETL, while blocking the other type, as well as protecting the perovskite layer from moisture or air penetration, thereby improving device efficiency and stability.

4. Charge Transport Layers

The HTL is a p-type material, which plays a crucial role in the selective extraction of photogenerated holes from the perovskite layer and transports them to the collecting electrode, as well as providing a good ohmic contact between the perovskite active layer and the collecting electrode. Hence, an effective HTL should have proper energy level alignment, in which its work function is close to the valence band edge of the perovskite material, for the efficient extraction and transportation of holes, and low electron affinity for the effective blocking of electrons, thereby suppressing charge carrier recombination. The HTL should also seal the perovskite layer from moisture penetration and prevent the electrode material, e.g., ITO, from diffusing into the perovskite layer, together with having high thermal stability to inhibit device degradation, and low cost, to promote commercialization of PSCs.

The p-type organic hole conductor, spiro-OMeTAD, has been most commonly used as the HTL in state-of-the-art PSCs due to its ability to deliver a high PCE. However, spiro-OMeTAD is expensive and has poor stability. Also, pristine spiro-OMeTAD has a low intrinsic charge carrier mobility, hence, it often requires the introduction of p-type dopants, such as tert-butylpyridine (tBP), Li-bis(trifluoromethanesulfonylimide (Li-TFSI), and co-complexes to improve its electrical conductivity. However, the corrosive and hygroscopic nature of the dopants leads to the introduction of moisture into the perovskite active layer, which subsequently reduces device performance and long-term stability.

As a result, several p-type conductive polymers, such as poly(triarylamine) (PTAA) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), have been extensively investigated as potential HTLs in PSCs due to their competitive optical and electrical properties. Among these, PTAA has a high work function of $\approx 5.4$ eV, which produces better energy level alignment with the valence band edge of the perovskite.
lead halide perovskites, thereby forming a good ohmic contact at the HTL/perovskite interface,[46] resulting in effective hole extraction and efficient hole transport. However, the use of PTAA is limited by its high cost and severe wettability challenges when depositing the perovskite layer.[176] hence calling for more research on PSC HTLs.

On the other hand, PEDOT:PSS has merits of low-temperature solution processability, high visible optical transmittance, moderate electrical conductivity, and flexibility, coupled with its ability to smooth out the ITO or FTO surface, which minimizes undesirable effects, such as short circuits, leakage current, and carrier recombination, that usually emanate from the rough ITO or FTO surface.[99] Nonetheless, PEDOT:PSS has a much lower work function of \( \approx 4.8 - 5.2 \) eV when compared with \( \approx 5.3 - 5.8 \) eV for the valence band edge of the lead halide perovskites.[46,177,178] This produces an unfavorable energy band mismatch, which causes energy losses during hole extraction, hence hindering the efficient collection of holes at the HTL/perovskite interface and resulting in poor device performance.[179,180] PEDOT:PSS is also highly acidic and hygroscopic, which results in corrosion of the ITO electrodes and diffusion of water or oxygen into the perovskite active layer, thereby causing poor device performance and severe instability.[181] In addition, PEDOT:PSS has poor electron-blocking capabilities as well as structural and electrical inhomogeneity, which renders it with a relatively low electrical conductivity of \( \approx 10^{-3} \, \text{S} \, \text{m}^{-1} \) due to the insulating nature of PSS.[182] Hence, future research on less corrosive HTLs is required to suppress the HTL-induced corrosion of the ITO and perovskite layers, which improves the device’s stability.[169]

Thus, the stability against heat and moisture of several metal oxides, such as nickel(II) oxide (NiO)[183] and copper oxides (CuO)[46] and inorganic salts, such as copper iodide (CuI)[47] and copper(I) thiocyanate (CuSCN)[184] have rendered them with ample potential to replace or modify spiro-OMeTAD and PEDOT:PSS. Recently, carbon-based materials, in particular, graphene and its derivatives, have emerged as promising HTL alternatives in PSCs, due to their advantages of low cost, solution processability, a high optical transparency, electrical conductivity, and electron blocking capability, in addition to superior stability and excellent flexibility.[185,186]

In this regard, Wang et al.[169] used ammonia-treated GO (a-GO) as an HTL in p-i-n-type MAPbI\(_3-x\)Cl\(_x\) planar PSCs. This enhanced the energy level alignment at the interface between the a-GO HTL and the perovskite layer, thereby giving rise to effective hole transport, which, in turn, increased the \( J_{sc} \) and FF, resulting in a relatively high PCE of 14.14%, when compared with the pristine GO- and PEDOT:PSS-based devices, which had PCEs of 11.97% and 12.58%, respectively. In addition, the a-GO- and GO-based devices managed to retain above 90% and \( \approx 80\% \) of their original PCE, respectively, as shown in Figure 8a, after storage for 30 days under a nitrogen atmosphere, demonstrating their ability to suppress the corrosion of ITO electrodes and, hence, their excellent long-term stability. Therefore, a-GO can be used in future research as a noncorrosive HTL for the fabrication of highly efficient and more stable devices.

In separate studies, Selvakumar et al.[187] Chowdhury et al.[188] and Ding et al.[189] respectively, used boron (B)-doped rGO, rGO/CuSCN, and rGO/NiO as HTLs in MAPbI\(_3\)-based PSCs. This improved the band matching of the perovskite layer and counter electrode, thereby enhancing hole extraction, hole mobility, and the \( J_{sc} \), resulting in B-rGO-, rGO/CuSCN-, and rGO/NiO-based PSCs with PCEs of 8.96%, 14.28%, and 8.50%, respectively, which outperformed the pristine rGO-based devices. More importantly, the rGO-based devices displayed excellent long-term operational stability, as revealed, e.g., by the ability of the rGO/CuSCN-based PSCs to retain \( \approx 90\% \) of their original PCE after continuous light soaking for 100 h,[50] as shown in Figure 8b.

A further step was made by incorporating rGO into the conventional PEDOT:PSS[95] and spiro-OMeTAD[49,188] HTLs of PSCs, as shown in Figure 9. This increased the work function of the composite HTLs and, hence, improved the energy level matching between the perovskite layer and the HTL, as shown in Figure 9a, which increased the built-in potential and electrical conductivity for effective hole extraction and transportation, with minimum recombination. This resulted in devices with PCEs of 16.01%, 18.13%, and 19.30%, respectively, which outperformed the pristine PEDOT:PSS-, spiro-OMeTAD-, and rGO-based PSCs. The poor performance of pristine rGO-based devices was ascribed to the relatively rough surface morphology of pristine rGO HTLs, which acted as a source of short circuits and leakage current that impaired device performance. More importantly, the devices based on composite HTLs displayed excellent long-term environmental stability. For example, the rGO/spiro-OMeTAD-based PSCs managed to retain \( \approx 75\% \)[189]

Figure 8. The variation of a) normalized PCE of a-GO- and GO-based PSCs with storage time. Adapted with permission.[169] Copyright 2019, Elsevier. b) The variation of PCE of rGO-, CuSCN-, and rGO/CuSCN-based PSCs with storage time. Adapted with permission.[50] Copyright 2018, Elsevier.
and above 97%\(^{[45]}\) of their initial PCE after storage for 500 and 700 h, respectively, under environmental conditions, thereby demonstrating the potential of graphene-based HTLs in addressing the poor stability issues of PSCs. Hence, as a future research direction, the integration of graphene-based materials with the traditional charge transport layers is beneficial to next-generation device fabrication, because it not only increases the efficiency of PSCs, but also protects the perovskite layer from moisture or oxygen penetration and ion migration, thereby improving the device’s stability.

The superior optoelectronic properties and stability of graphene to rGO and GO have also led to the application of graphene as a HTL in PSCs.\(^{[190]}\) Although the \(J_{sc}\) of the graphene HTL-based PSCs was higher than that of the spiro-OMeTAD devices, the relatively low \(V_{oc}\) and FF of the graphene-based PSCs gave rise to a lower PCE of 7.1%, when compared with 12.6% for the spiro-OMeTAD-based control device. However, the graphene-based devices managed to retain \(\sim 80\%\) of the original PCE after continuous irradiation for 1 h under environmental conditions, in comparison with the spiro-OMeTAD reference devices, which dropped almost all the initial PCEs under the same conditions. This was ascribed to the chemical inertness and hydrophobicity of the graphene layer, which prevented the diffusion of water and oxygen molecules into the perovskite active layer. Hence, future optimization of the efficiency of graphene-based devices, while maintaining their superior stability, would make the commercialization of PSCs a success. This was comparable to a previous study,\(^{[191]}\) in which iodine (I\(_2\))-doped nanocomposites of graphene with conducting polymers, such as PEDOT and polythiophene (PTh), were used as HTLs in PSCs, to enhance hole extraction and transport, resulting in devices with PCEs of 8.79% and 4.95%, respectively. Interestingly, the I\(_2\)-doped PEDOT/graphene and I\(_2\)-doped PTh/graphene-based PSCs displayed only a small drop in PCE to 6.38% and 4.60% after 180 days of storage under environmental conditions, indicating their excellent long-term environmental stability.

Recently, GQDs,\(^{[119]}\) PEDOT:PSS/GQDs,\(^{[192]}\) and ammonia-treated GQDs (a-GQDs)/NiO\(_{x}\)\(^{[193]}\) have been used as HTLs in p-i-n-type PSCs, which displayed PCEs of 17.15%, 16.16%, and 19.40%, respectively. Although pristine GQDs-based PSCs exhibited relatively lower PCEs than 17.55% for the PEDOT:PSS control device, they only dropped 28% of the original PCE after 30 days of storage in a \(N_2\) environment, as compared with the 42% drop for the PEDOT:PSS-based device.\(^{[119]}\) Also, the PEDOT:PSS/GQDs-based devices outperformed the pristine PEDOT:PSS-based devices due to the well-matched work function, improved hole extraction, efficient hole mobility, and selective electron-blocking capabilities of the PEDOT:PSS/GQD nanocomposites, which suppressed charge carrier recombination, resulting in an enhanced \(J_{sc}\), and subsequently high device efficiency.

Interestingly, the PEDOT:PSS/GQDs-based PSCs managed to retain 77% of the original PCE after storage for 9 days under environmental conditions, in comparison with the pristine PEDOT:PSS reference devices, which maintained 58% of the initial PCE under the same conditions.\(^{[192]}\) The poor stability of PEDOT:PSS-based devices was attributed to corrosion of the transparent conductive electrodes due to the acidic and hygroscopic nature of PEDOT:PSS, which leads to the diffusion of metal ions into the perovskite active layer, thereby degrading the perovskite active layer. Also, the a-GQDs/NiO\(_{x}\)-based PSCs outperformed the pristine NiO\(_{x}\)-based devices that had a PCE of 17.4%.\(^{[193]}\) In addition to the excellent environmental stability, revealed by the ability to retain 74% of the initial PCE after exposure to air for 30 days without encapsulation, the a-GQDs/NiO\(_{x}\)-based devices managed to maintain 88% of the original PCE after 1000 bending cycles, indicating their superior mechanical stability. Hence, it is envisaged that with future research, the efficiency of PSCs using GQD-based HTLs could be further improved, without sacrificing the stability, e.g., via the preparation of novel GQD nanocomposites and doping.

A summary of the photovoltaic parameters of PSCs that incorporated graphene-based HTLs, discussed in this review, is presented in Table 4. Among these, devices with the rGO/spiro-OMeTAD\(^{[45]}\) and a-GQDs/NiO\(_{x}\)\(^{[193]}\) HTLs displayed excellent stability and outstanding efficiency of above 19%. Hence, with continuous research effort, the hole extraction, transportation, and collection capabilities of graphene-based HTLs can be significantly improved, while at the same time using the graphene-based HTLs as protective layers to prevent the rapid degradation of the perovskite active layer materials. This subsequently improves the efficiency and long-term stability of PSCs, which is a remarkable step toward commercialization.
4.2. Electron Transport Layer

The ETL is responsible for extracting electrons from the perovskite layer and transporting them to the collecting electrode, while blocking hole transport,\textsuperscript{[194,195]} thereby suppressing charge carrier recombination and, hence, improving device efficiency. Therefore, an effective ETL should have a matching energy band, where its work function is slightly lower than the conduction band of the perovskite material for the effective extraction of electrons and high electron mobility for the efficient transportation of electrons.\textsuperscript{[196]} Thus, a good ETL should provide a better ohmic contact at the perovskite layer–electrode interface, to improve the device performance. Also, an appropriate ETL should be hydrophobic and chemically stable, for it to be moisture resistant and prevent undesirable chemical reactions with the perovskite and electrode materials, which improves the device’s stability.

The n-type metal oxide semiconductors, such as \( \text{TiO}_2 \),\textsuperscript{[197]} zinc oxide (\( \text{ZnO} \)),\textsuperscript{[198]} tin dioxide (\( \text{SnO}_2 \)),\textsuperscript{[199]} tungsten trioxide (\( \text{WO}_3 \)),\textsuperscript{[200]} niobium pentoxide (\( \text{Nb}_2\text{O}_5 \)),\textsuperscript{[201]} and aluminum oxide (\( \text{Al}_2\text{O}_3 \))\textsuperscript{[202]} have been used as ETLs in PSCs. Among these, \( \text{TiO}_2 \) has been most commonly used as the conventional ETL due to its low cost, simple fabrication procedures, environmental friendliness, high optical transparency, and matched energy levels with those of most perovskite materials.\textsuperscript{[203-205]} Nonetheless, the sensitivity of \( \text{TiO}_2 \) to UV illumination causes poor stability, whereas its low electron mobility leads to poor electron transport, resulting in charge carrier recombination and low electrical conductivity, which impairs device performance and, hence, limits the commercial application of \( \text{TiO}_2 \).\textsuperscript{[196]} Also, the high-temperature sintering process required to enhance the crystallinity and electron mobility of \( \text{TiO}_2 \) consumes more energy and is not compatible with flexible substrates.\textsuperscript{[206]}

Recently, carbon-based materials, including CNTs, graphene, and fullerene-based n-type semiconductor materials, such as [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) and C\(_{60}\),\textsuperscript{[200,207]} have been used as alternative ETLs in PSCs due to their competitive optical and electronic properties. Among these, graphene-based materials have attracted considerable research interest as low-cost alternative ETLs owing to their unique properties, such as solution processability, high electron mobility, high optical transparency, good electrical conductivity, excellent stability, and flexibility, coupled with their hydrophobicity, which prevents the absorption of moisture, thereby improving the device’s stability.

In this respect, composites of rGO with metal oxide semiconductors, such as \( \text{SnO}_2 \)\textsuperscript{[208]} and \( \text{TiO}_2 \)\textsuperscript{[209]} have been used as ETLs in n-i-p-type PSCs. This increased the electron mobility and suppressed charge carrier recombination, which subsequently improved the PCE from 13.90% and 14.39% for the pristine \( \text{SnO}_2 \)- and \( \text{TiO}_2 \)-based devices, respectively, to 16.87% and 17.66% for the corresponding devices with \( \text{rGO-SnO}_2 \) and \( \text{rGO-TiO}_2 \) ETLs. In addition, the rGO-metal oxide semiconductor composite ETLs resulted in devices with excellent long-term stability, e.g., as revealed by the ability of the rGO-SnO\(_2\)-based PSCs to retain \( \approx \)80% of the initial PCE after storage in a glove box without encapsulation for 300 h, when compared with their pristine \( \text{SnO}_2 \) counterparts, which retained less than 50% of the original PCE under the same conditions.\textsuperscript{[208]} Recently, rGO-TiO\(_2\) composites have been used as ETLs in MAPbI\(_3\) and rGO-MAPbI\(_3\) active layer-based PSCs, which exhibited PCEs of 15.3% and 16.5%, respectively.\textsuperscript{[163]} This outperformed the reference devices based on the TiO\(_2\) ETL, which had a PCE of 13.8%. Interestingly, the rGO-based PSCs managed to retain 40% of the original PCE after storage for 50 days, under mildly humid and dark conditions, as compared with the rGO-free devices, i.e., TiO\(_2\) ETL reference devices, which retained only 20% of the initial PCE under the same conditions. This demonstrates that the introduction of rGO into the ETL not only improves the device efficiency, but also provides a passivation effect at the interface, which enhances the device’s stability.

The superior optoelectronic properties of graphene to rGO, and extremely high electron mobility and stability of graphene than TiO\(_2\), enabled graphene to be incorporated into TiO\(_2\) and to be used as a composite ETL in PSCs,\textsuperscript{[210]} as shown in Figure 10a. This resulted in better electron extraction than with pristine TiO\(_2\) due to proper energy level alignment between the graphene-TiO\(_2\) ETL and the perovskite layer and, hence, reduced the energy barrier, because the work function of graphene lies between that of FTO and the conduction band of TiO\(_2\). Also, the introduction of graphene into the ETL provided highly conductive electron transport pathways, which suppressed charge carrier recombination and prolonged the electron lifetime, resulting in a high \( J_{sc} \) as shown in Figure 10b. This resulted in PCEs of 16.03% and 17.01% for the PSCs with pristine graphene and graphene-TiO\(_2\) composite ETLs, respectively, when compared with 14.42% for the reference TiO\(_2\) ETL-based devices. A further increase in PCE to 17.94% was observed by replacing the CuSCN HTL with NiO, demonstrating that with continuous optimization of all the device components, favorable device performance could eventually be achieved in the near future.
Recently, graphene/ZnO$^{[211]}$ and nitrogen-doped graphene/ZnO nanorod (N-graphene/ZnO NR) nanocomposites$^{[212]}$ have been used as ETLs in highly efficient and stable n-i-p PSCs. The wide bandgap of ZnO usually facilitates the formation of an effective hole-blocking layer, and the matched energy levels of graphene/ZnO and N-graphene/ZnO with those of the perovskite layer promote the rapid extraction of electrons with minimum recombination. Moreover, the introduction of graphene and N-graphene into the ETL provides highly conductive electron transport pathways, which reduce the interfacial resistance, suppress charge carrier recombination, and increase the electron lifetime, FF, and $J_{SC}$. As a result, the graphene/ZnO- and N-graphene/ZnO NR-based devices showed the optimum PCEs of 21.03% and 16.82%, respectively, which outperformed the ZnO reference devices, demonstrating the significance of using graphene-based nanocomposites and doping as efficient approaches to prepare future ETL materials for high-performance PSCs. Also, the graphene-based PSCs displayed excellent stability, as revealed by the ability of the graphene/ZnO-based devices to maintain $\approx$93% of their initial PCE after continuous illumination for 300 h, hence paving the way for the commercialization of PSCs.

GQDs have also been integrated with metal oxide semiconductors, such as TiO$_2$,$^{[48,213,214]}$ ZnO$^{[215]}$ and SnO$_2$,$^{[216]}$ and the resulting GQD-TiO$_2$, GQD-ZnO, and GQD-SnO$_2$ nanocomposites were used as ETLs in n-i-p PSCs. The introduction of GQDs onto the surface of the metal oxide semiconductors not only enhanced the extraction of electrons but also reduced the contact resistance at the perovskite layer/ETL interface, which lowered the series resistance and improved the transportation of electrons at the perovskite layer/ETL interface, thereby increasing the $J_{SC}$ and $V_{OC}$. The incorporation of highly conductive GQDs into the metal oxide semiconductor ETLs also suppressed charge carrier recombination and significantly reduced the leakage current, which increased the shunt resistance and FF. This resulted in GQD-TiO$_2$-based devices with PCEs of 20.45%,$^{[211]}$ 14.36%,$^{[48]}$ and 11.74%,$^{[214]}$ GQD-ZnO-based devices with a PCE of 17.63%,$^{[215]}$ and GQD-SnO$_2$-based devices with a PCE of 21.10%,$^{[216]}$ which outperformed the pristine metal oxide semiconductor reference devices.

Most importantly, the devices based on GQD-TiO$_2$ ETLs managed to retain $\approx$88% of their original PCE after storage for 500 h under environmental conditions, as compared with the pristine TiO$_2$ reference devices, which retained only 61% of the original PCE under the same conditions.$^{[48]}$ On the other hand, the GQD-ZnO-based devices only dropped $\approx$20% of their initial PCE after storage under 60% relative humidity for 1500 h, when compared with the pristine ZnO references devices, which lost $\approx$75% of the original PCE under the same conditions.$^{[215]}$ In addition, the devices based on GQD-SnO$_2$ ETLs maintained $\approx$80% of their initial PCE after storage for 720 h (30 days) under environmental conditions, in comparison with the pristine SnO$_2$ reference devices, which maintained only 65% of the initial PCE under the same conditions.$^{[216]}$ as shown in Figure 11. GQDs have also been incorporated into PCBM, resulting in more stable PSCs with a high PCE of 16.41%.$^{[120]}$ This reveals the significance of using GQDs in future research, as additives to the traditional ETL materials, to improve not only the efficiency, but also the long-term environmental stability of devices, which are both indispensable for commercial applications.

The photovoltaic parameters of PSCs with graphene-based ETLs, discussed in this review, are summarized in Table 5. Among these, devices with graphene/ZnO$^{[211]}$ GQD-TiO$_2$,$^{[213]}$ and GQD-SnO$_2$ ETLs displayed excellent stability and best PCEs of 21.03%, 20.45%, and 21.10%, respectively, indicating...
that with further research effort, graphene-based ETL materials could eventually produce high-performance and sustainable PSCs.

5. External Encapsulation

Although the PCE of PSCs is now comparable to that of silicon-based solar cells, the commercialization of PSCs is mainly limited by their poor long-term environmental stability, emanating from the instability of the most commonly used perovskite materials as electrodes, HTLs, and ETLs, upon exposure to heat, UV radiation, oxygen, or moisture from the environment.[217-219] Besides controlling the internal degradation mechanisms of PSCs with good choices of stable electrodes, charge transport layers, and active layers, external encapsulation has been proposed as another promising approach for protecting devices against direct exposure to UV radiation, heat, and moisture, thereby enhancing the long-term environmental stability of PSCs, while maintaining high efficiency.[217] As a result, several materials, including Al₂O₃, polyisobutylene, Teflon, and poly(methyl methacrylate) (PMMA),[218,220,221] have been used as encapsulation layers on top of the counter electrodes in PSCs, to create a hydrophobic and thermally conductive shield. Recently, the hydrophobicity and high thermal conductivity of carbonaceous materials, particularly graphene and its derivatives, have enabled them to be used as encapsulants for effectively blocking moisture or oxygen in the surrounding environment and to dissipate heat through the encapsulation layer, thereby lowering the device temperature during operation.[145]

Being motivated by the recent drive toward the commercial application of PSCs, some researchers have used PMMA/rGO, rGO, and graphene as external encapsulation layers in PSCs,[222-224] as shown in Figure 12. The PMMA/rGO, rGO, and graphene-encapsulated devices displayed a negligible drop in efficiency and, respectively, managed to retain ≈90%, 95%, and 82% of the original PCE, after storage for 500, 1000, and 3700 h, under environmental conditions. This demonstrated the effective moisture and oxygen blocking capabilities of graphene-based materials, when compared with the graphene-free devices, which showed a rapid drop in PCE under the same conditions. In addition, the rapid dissipation of heat through the thermally conductive PMMA/rGO, rGO, and graphene encapsulation layers played a significant role in reducing thermal damage of PSCs at high temperatures, thereby enhancing the thermal stability of the devices. Therefore, the strong resistance of graphene-based materials to moisture, heat, and UV radiation is envisaged to help in addressing the instability issues in PSCs, hence opening up avenues for the commercial application of PSCs. Thus, this work paves the way for future research to focus not only on controlling the internal degradation mechanisms of PSCs, but also to concentrate on external encapsulation, as a way of improving the stability and, hence, prolonging the lifetime of graphene-based PSCs.

6. Conclusion and Outlook

In this review, the recent breakthroughs in the application of graphene-based materials in electrodes, active layers, charge transport layers, and encapsulation layers of PSCs have been presented, with a major focus on the photovoltaic parameters. Although PSCs have shown a rapid increase in PCE over the past few years, with current values now approaching those of silicon-based solar cells, the commercialization of PSCs is still limited by their poor long-term stability. In this regard, there has been significant research interest in developing more robust and novel materials for the fabrication of various components of PSCs, such as electrodes, active layers, charge transport layers, and encapsulation layers, so as to enhance not only the efficiency, but also the long-term stability of PSCs. Among the promising alternative materials, carbon-based materials, in particular, graphene and its derivatives, have gained considerable research attention owing to their remarkable optoelectronic, mechanical, thermal, and chemical properties, together with their low cost, solution-processability, elemental abundance, and less impact on the environment. Most importantly, the high optical transparency, high electrical conductivity, and selective charge carrier

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Table 5. Photovoltaic parameters of PSCs with graphene-based ETL materials.

| ETL            | V oc [V] | J sc [mA cm⁻²] | FF  | PCE [%] | References |
|----------------|----------|----------------|-----|--------|------------|
| rGO-SnO₂       | 1.05     | 22.57          | 0.73| 16.87  | [208]      |
| rGO-TiO₂       | 1.07     | 22.16          | 0.75| 17.66  | [209]      |
| rGO-TiO₂       | 1.01     | 21.40          | 0.71| 15.30  | [163]      |
| rGO-TiO₂       | 1.00     | 22.90          | 0.72| 16.48  | [163]      |
| Graphene TiO₂  | 1.15     | 18.66          | 0.84| 17.94  | [210]      |
| Graphene       | 0.89     | 21.73          | 0.83| 14.42  | [210]      |
| Graphene/ZnO   | 1.15     | 23.42          | 0.78| 21.03  | [211]      |
| N-graphene/ZnO NR | 1.02  | 21.98          | 0.75| 16.82  | [212]      |
| GQD-TiO₂       | 1.08     | 24.92          | 0.76| 20.45  | [213]      |
| GQD-TiO₂       | 0.97     | 21.92          | 0.67| 14.36  | [48]       |
| GQD-TiO₂       | 0.83     | 22.10          | 0.64| 11.74  | [214]      |
| GQD-ZnO        | 1.02     | 24.70          | 0.70| 17.63  | [215]      |
| GQD-SnO₂       | 1.11     | 24.40          | 0.78| 21.10  | [216]      |
| GQD-PCBM       | 1.07     | 20.75          | 0.74| 16.41  | [120]      |

![Figure 12. Schematic diagram of a PSC based on a PMMA/rGO external encapsulation layer.](https://www.advancedsciencenews.com)
blocking capability of graphene-based materials facilitate their use as transparent conductive electrodes and charge transport layers in PSCs. Furthermore, the unique 2D packed network, chemical inertness, and hydrophobicity of graphene enhance the device’s long-term stability. Therefore, as a future research direction, the stability of the various device components can be enhanced, while maintaining high efficiency, using several approaches, such as doping, preparation of graphene-based nanocomposites, interface engineering, and encapsulation. If done, this is envisaged to pave the way for the future realization of low-cost, high-performance, and sustainable graphene-based PSCs, which is a remarkable step toward commercial application.

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Conflict of Interest
The authors declare no conflict of interest.

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active layers, charge transport layers, graphene, perovskite solar cells, transparent conductive electrodes

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