The efficiency of graphene and its derivatives in perovskite solar cells: A review

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***Abstract*: Perovskite solar cells (PSCs) are rapidly emerging as the most promising photovoltaic technology, gaining attention on the global energy scene and attracting efforts of the scientific community to develop efficient and stable perovskite-based devices. Hybrid perovskite-graphene solar cells show good stability upon exposure to sunlight, while still maintaining efficiency of over 18%. With the constant increase in the efficiency and stability of PSCs in recent years, the research on graphene-based photovoltaic cells pushes forward the commercialization of PSCs step by step. This review introduces the advances in PSCs along with the properties of graphene and summarises their applications further. Moreover, a brief discussion on Graphene Quantum Dots (GQDs) and prospects for the further development of graphene and its applications in PSCs are discussed.**

***Keywords*: Graphene, GQDs, Perovskites, PSCs, Derivatives, Solar cells**

1. Introduction

With the increasing global energy consumption and the demand for green energy technologies, traditional energy sources struggle to meet the current sustainable development needs of human society. To overcome this problem, researchers have made great efforts to explore alternative materials for next-generation photovoltaics. Lately, perovskite solar cells have attracted widespread attention as they have become a promising thin-film photovoltaic technology due to their high light-absorption coefficient, high charge mobility, and long carrier diffusion length. Recently, graphene, an allotrope of carbon in the form of a plane of sp2-bonded atoms, has been used as a novel material for PSC applications due to its excellent optical, electrical, and mechanical properties, also providing better energy level alignment, leading to more efficient devices. At present, PSCs have generated broad interest because of their rapid PCE improvement from 3.8% in 2009 to 22.1% in 2016, as shown in **Fig.1.** In addition, PSCs also have prominent advantages such as being lightweight, having a low cost of manufacturing, high efficiency rate, and flexibility. Besides the increasing efficiency, the long-term stability of PSCs against light, damp climate conditions, and heat also improved significantly in recent years. The latest survey has shown that 90% of photovoltaic products on the global market are based on first-generation silicon (Si). Even though it was employed as the first material to manufacture Solar cells but its disadvantages are high cost and lower efficiency whereas PSCs cost less and promise great outcomes. Silicon panels are also not ideal for transportation since their structure is quite fragile and rigid. Perovskite solar cells have a standard structure, including the type of materials that are used in their manufacturing and composition, so the substitution of one material for another seems like a comparatively simple process that leads to highly tunable and durable solar cell devices. The integration of graphene and its derivatives into PSCs has been extensively proved with a positive effect on PSC performance improvement and device stability over the years.

Herein, we review the advances in perovskite cells along with the important role that graphene and its derivatives play in PSCs. Initially, the electronic and optical properties of graphene and its derivatives are discussed. Finally, the perspectives and opportunities for graphene and its derivatives and its limitations in highly efficient and stable PSCs are reviewed.

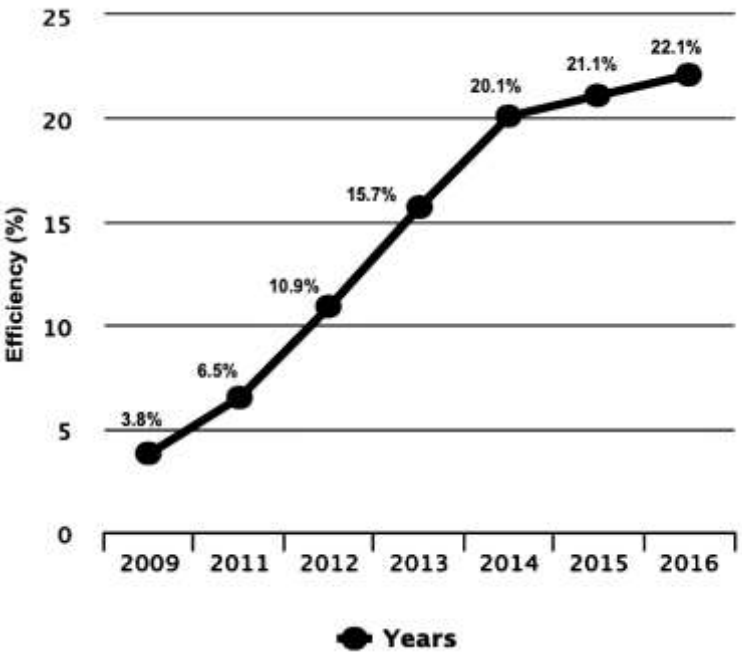

Fig. 1. PCE improvement rate of PSCs from 2009 to 2016

2. Advances in Perovskite Solar Cells

Halide perovskites are a family of materials that have shown potential for high performance and low production costs in solar cells. Solar panels made from perovskites could change how we generate electricity, opening the door to flexible and even transparent solar panels. Perovskite solar cells have drawn significant attention from researchers from both academia and industry. PSCs are mainly composed of perovskite absorbers, counter electrodes, and charge transport layers. The energy loss in the bulk and interface of perovskite layers, and the charge extraction and transportation process in the device play a critically significant role in determining the efficiency of these solar cells. For photovoltaic energy to become competitive with fossil fuels and to capture a significant share of the electricity market, it is necessary to reduce the total cost of solar energy. This can be achieved by either reducing the cost of photovoltaic cells or by increasing their power conversion efficiencies. Silicon is currently widely used in the production of perovskite-based photovoltaic cells, but while silicon cells are very expensive to produce, graphene-based cells potentially cost much less in comparison. When materials such as silicon turn light into electricity it produces a photon for every electron produced, i.e., a lot of potential energy is lost as heat whereas when graphene absorbs a photon, it generates multiple electrons. The hydrophobic nature of graphene enhances several properties of perovskite solar cells such as stability and the passivation of electron traps at the perovskite's crystalline domain interfaces. Perovskite is a compound that has an ABX3 stoichiometry structure, where A and B are 12- and 8-coordinates cations, respectively, and X is the anion. Of the many ABX3 compounds, only a few are suitable to be efficient light absorbers for solar cells due to requirements such as appropriate bandgap for good light-harvesting ability and long charge carrier lifetime. PSCs exhibit high performance when using active areas of about 1 cm2. The large-scale production of solar cells is crucial for their commercial use. They mainly consist of thin layers of several materials, each playing a different role in the conversion of light to electrical power. In the perovskite layer, solar energy is converted to free charges, which travel through the cell to produce electricity. A big advantage PSCs have is that they can react to various different wavelengths of light, which lets them convert more of the sunlight that reaches them into electricity, enabling further advancement of the power conversion efficiency beyond those afforded by the silicon solar cells.

3. Electrical and optical properties of graphene

Graphene is a single layer of atoms arranged in a two-dimensional honeycomb lattice nanostructure, as shown in **Fig. 2(a).** Graphene's flat honeycomb pattern gives it many extraordinary characteristics, such as being the strongest material in the world, as well as one of the lightest, most conductive and transparent.

Most polymers have a low conductivity of around 10−10 S/m, while the conductivity of graphene can be as high as 104–105 S/m. Reported results have shown that graphene possesses high thermal conductivity of -5 * 10^3 W m^{-1} K^{-1} at room temperature and high optical transparency of 97.7% in the infrared to ultraviolet region. A single sheet of graphene, in which each sheet is viewed as a solitary particle is a zero-band gap semiconductor with very high carrier mobilities that can only absorb 2.3% of visible light. Hence, graphene may be a viable candidate for applications as a transparent conductor. Graphene derivatives – graphene oxide (GO) and reduced graphene oxide (rGO**) Fig. 2(b)** – in aqueous solutions are also attractive for many potential applications such as printed electrodes, solar cells, flexible electronic devices, and biosensors. Reduced graphene oxide is a single-layered sheet that is derived from the chemical reduction of graphene oxide. Graphene is the only crystal that can be stretched by 20%, thus enhancing the working range of sensors and flexible electronic devices significantly. Graphene oxide has a mixture of sp^2 and sp^3 hybridized

carbon atoms that are covalently bonded to oxygen-containing functional groups on the basal plane. These functional groups enable graphene oxide (GO) to exhibit properties such as hydrophilicity and water solubility alongside providing sites for the immobilization of various biomolecules through covalent bonds. Graphene can also produce optical transitions in an electric field which are also known as gate-dependent optical transitions. Combined research over the last 50 years has proved that at the Dirac point in graphene, electrons and holes have zero effective mass. This occurs because the energy–movement relation is linear for low energies near the 6 individual corners of the Brillouin zone. Under the influence of an applied electrical field, the low density of states near the Dirac point tends to cause the Fermi level of graphene to shift significantly. A change in the Fermi level has a major effect on conductivity and on the process of tuning the transmission of an optical source. This process is often used in electronics to modulate current levels. These modulations are performed by the material absorbing electromagnetic radiation, which in this case is infrared radiation; this dictates how much radiation is absorbed by graphene.
Thus, graphene has tremendous application potential in wearable sensors, optical modulators, photoelectric fields, etc.

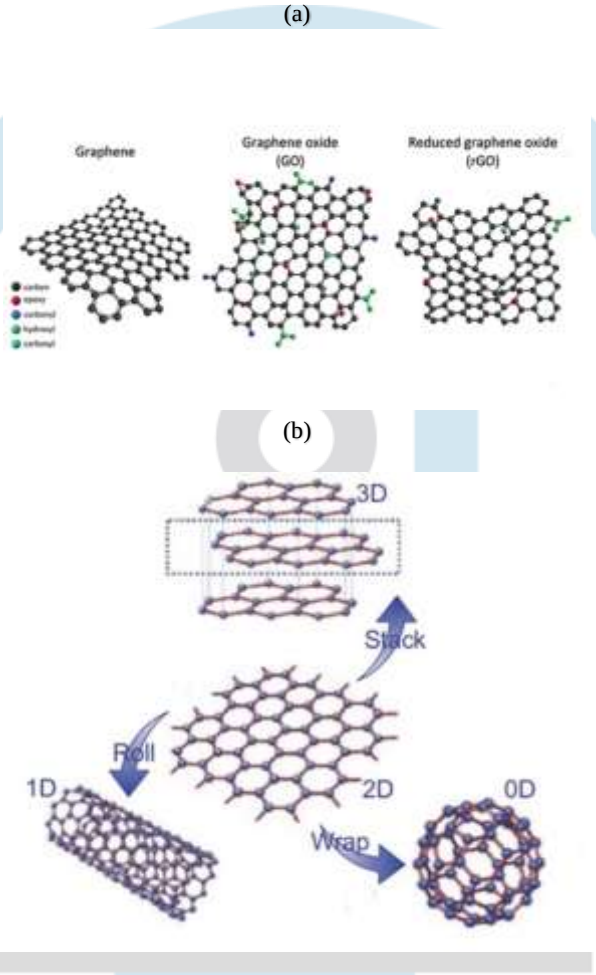

Fig. 2. (a) Graphene and its derivates(GO and rGO) (b) The lattice structure of 2D graphene and its derived structures

4. Graphene Quantum Dots

A quantum dot solar cell (QDSC) is a solar cell design that aims to use quantum dots as the absorbing photovoltaic material. GQDs are chemically and physically stable because of their intrinsic inert carbon property. The main idea of QDSCs is to replace bulk materials such as silicon, CIGS, or cadmium telluride (CdTe).
Graphene quantum dots (GQDs) are graphene nanoparticles with a size less than 100 nm that have attracted a great deal of attention in photovoltaic applications due to a series of excellent properties such as low toxicity, chemical stability, high carrier transport mobility, large surface area, quantum confinement, etc. Both graphene and carbon nanotubes have been hybridized with quantum dots in order to make functioning solar cells. Of the two carbon allotropes, graphene hybridized quantum dots have displayed immense potential. GQDs can also be combined with other materials to produce nanocomposites with remarkable properties and superior performance. Quantum dots (QDs) are semiconductor nanocrystals with a core-shell structure and a diameter that typically ranges from 2 to 10 nm. The core of QDs is usually composed of elements from groups II-VI such as CdSe, CdS, or CdTe, groups III–V such as InP or InAs, or groups IV-VI such as PbSe. The synthesis of graphene quantum structures(shown in **Fig.3(a)**), such as graphene quantum dots, has become a popular topic in recent years. While graphene usually does not have a bandgap - which may pose itself as a problem for many applications - graphene quantum dots do contain a bandgap due to quantum confinement and edge effects, and that bandgap modifies graphene's carrier behaviours and can lead to versatile applications in photovoltaics. The GQDs are different from CDs because they possess a graphene lattice inside the dots, which are smaller than 100 nm in size

and less than 10 layers thick. CDs are usually quasi-spherical carbon nanoparticles having a size of less than 10 nm. The GQDs have many novel properties, such as their unique fluoresce due to their quantum confinement effect. The ability to modulate the properties of GQDs is important if the material is to be used in diverse applications. GQDs have also been very helpful in assessing the issue of instability in PSCs as shown in **Fig.3.(b).**

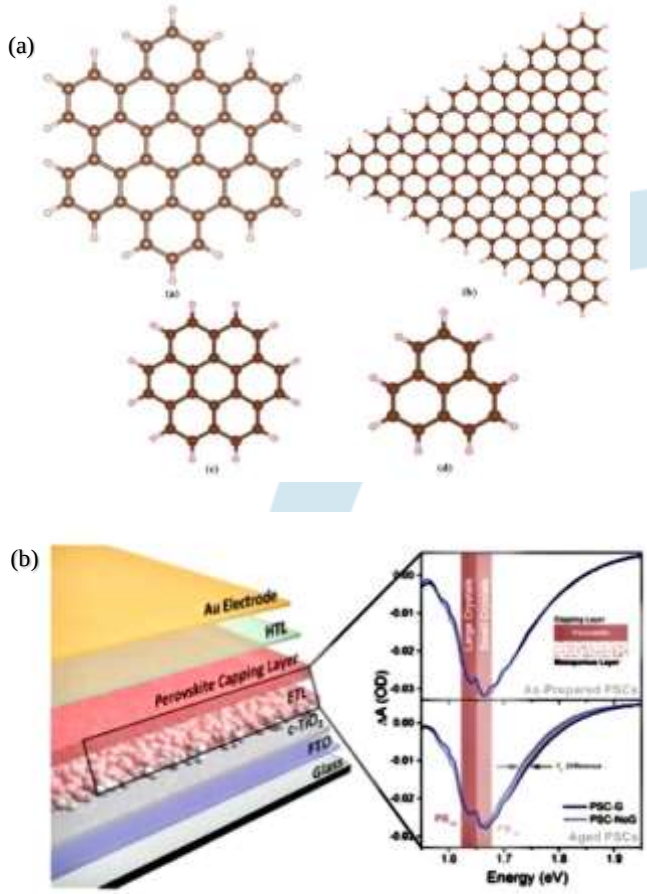

Fig. 3. (a) Schematics of various graphene quantum dots (GQDs) structures. (a) Hexagonal shape with armchair edges, (b) Triangular shape with an armchair edge, (c) Hexagonal shape with a zigzag edge, and (d) Triangular shape with zigzag edges. From "*Electronic Properties of Various Graphene Quantum Dot Structures: an Ab Initio Study", by Majid Ghandchi, G. Darvish, Mohammad Kazem Moravvej-Farshi, Tabriz Journal of Electrical Engineering (TJEE), vol. 51, no. 2, Summer 2021, © 2008-2022 ResearchGate GmbH"*
(b) Using quantum dot/graphene hybrids to address PSCs' instability issue.

5. Graphene as electron transport layers in PSCs

Electron transport layers (ETL) play a fundamental role in perovskite solar cells. The purpose of an electron transport layer between the active layer and the cathode (or the anode) is to reduce the recombination of the free charge carriers. Recently, graphene-based ETLs have been proved to be good candidates for scalable fabrication processes and to achieve higher carrier injection with respect to the most commonly used ETLs in PSCs. It was recently found that the carrier collection efficiency is increased by about a factor of two with respect to the standard TiO2 ETL. TIO2 is most commonly used as a compact electron transport layer due to its suitable band alignment. TiO2 has a homogenous layer with a small grain structure which helps enhance the surface area of the under-layer and plays a significant role in improving the net efficiency of the cells. Graphene's derivatives have also been demonstrated as transport layers in PSCs and the positive effects on the improvement of PSC performances have been demonstrated.

6. Limitations of PSCs

Despite its great potential, perovskite solar cell technology is still in the early stages of commercialization as there are still a number of concerns remaining. To increase stability, researchers are studying degradation in both the perovskite material itself and the surrounding device layers. Improved cell durability is critical for the development of commercial perovskite solar products. Producing uniform, high-performance perovskite material in a large-scale manufacturing environment is difficult, and there is a substantial difference in small-area cell efficiency and large-area module efficiency. The future of perovskite manufacturing will depend on solving this challenge, which remains an active area of work within the PV research community. Despite significant progress in understanding the stability and degradation of perovskite solar cells, they are not currently commercially viable because

of their limited operational lifetimes. One of the main downsides is the degradation issue of methyl ammonium lead iodide Perovskite which happens to be toxic. Researchers are exploring alternative ways to replace this toxic substance in PSCs. Another downside of perovskite solar cells is the film quality and thickness. The perovskite material will break down quickly due to exposure to heat, moisture, snow, etc.

Summary and Outlook

Recently, PSCs have become the most promising solar technology due to their impressively high rate of efficiency and stability. However, the great challenges of stability, scalability, and further enhancement of efficiency should be addressed in consideration of operational practice and industrial production of such photovoltaic devices. Therefore, the development of a high-stability device composition, including the light-absorbing layer, ETL/HTL, and electrode layer(GQDs/graphene), as well as the development of a simple and effective device-packaging method, will be of great significance to promote the practicability of such devices. In conclusion, graphene has been used as a conductive electrode, carrier transporting material, and stabilizer material for PSC applications and has produced promising results throughout the years.

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