

REVIEW

Recent insights into the transformative role of Graphene-based/TiO₂ electron transport layers for perovskite solar cells

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Abstract

Perovskite solar cells (PSCs) hold great promise for cost-effective and high-efficiency solar energy conversion. However, in practice, they face practical limitations due to suboptimal electron transport, inadequate hole-suppression, photocatalytic instability, and susceptibility to other environmental factors. Many transition metal oxides such as ZnO and TiO₂ have important excitonic properties that make them good electron transport layer (ETL) materials in PSCs. However, many of the PS limitations arise from inherent issues with these oxides. The high interest in TiO₂ is due to its low toxicity, chemical stability, and the potential to enhance its excitonic performance through doping with many materials. The main limitations of TiO₂ are its poor visible-light response by virtue of its wide bandgap of ~3.2 eV, and its high electron-hole (e-h) recombination rates, which are directly responsible for its low current densities. Transition metal oxide enhancements occur using either internal doping or surface sensitization. Of the added materials, graphene has exceptional electrical conductivity, high electron mobility, large surface area, and excellent mechanical properties, making it a near-ideal candidate to improve the performance of TiO₂. This review examines the important advances in graphene-TiO₂ (g-TiO₂) composites for ETL application. By forming a composite with TiO₂, graphene can significantly enhance electron transport, reduce recombination losses, and improve the overall stability of PSCs. We present the detailed rationale for and analysis of g-TiO₂ for improved electron transport efficiency, enhanced stability, and boosted overall PSC performance with the objective of providing an authoritative resource for the field.

KEYWORDS

graphene/TiO₂ electron transport layers, performance enhancement, Perovskite solar cells, solar energy conversion, stability challenge

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1 | INTRODUCTION

The world is in the grip of an energy and climate change crisis due to humanity's over-reliance on nonrenewable energy sources. As the race continues to find alternative energy solutions, the release of atmospheric greenhouse gases persists unabated. Solar energy, capable of meeting humanity's annual demand in just 1 h if optimally harnessed, presents a highly promising solution. The Earth continuously receives 174 Petawatts (PW) of incoming solar energy, which is convertible to electric power by solar photovoltaic (PV) cells.

PV cells have evolved significantly over time with key objectives of enhancing efficiency, reliability, and affordability. Continuous innovation in the PV field has led to the development of various generations of PV technologies, including crystalline silicon solar cells, thin-film solar cells, and other emerging technologies. Among these, perovskite solar cells (PSCs) stand out due to their high scalability and solution processability compared to silicon-based cells. This results in lower manufacturing costs and drives PSCs towards widespread adoption. Rapid improvements in their power conversion efficiencies (PCE)-to-cost ratios have outpaced other solar cell technologies. PSCs possess a distinct crystalline architecture that efficiently absorbs sunlight and enhances output currents, with properties that can be finely tuned and optimized through adjustments in chemical composition and structure, including bandgap, carrier mobility, and optical characteristics.

Despite their significant potential and advancements to date, the central issues faced by PSCs, namely sustained PCE performance, stability, production upscaling, and environmental toxicity are still far from settled.

Titanium dioxide (TiO_2) has been the most widely used ETL in PSCs because of its desirable properties. However, TiO_2 also exhibits several shortcomings, such as poor electrical conductivity, slow electron mobility, and photocatalytic instability, particularly at the TiO_2 /perovskite interface. These issues at the interface can lead to increased recombination losses and decreased efficiency. To address these limitations, researchers have explored various solutions, including the replacement of TiO_2 with other ETLs and the incorporation of additional compounds.

One of the most promising advancements is the incorporation of graphene with TiO_2 (g- TiO_2). Graphene's exceptional properties—such as superior electrical conductivity, high electron mobility, large surface area, and excellent mechanical strength—make it an ideal candidate to enhance the performance of TiO_2 . By forming a composite with TiO_2 , graphene can significantly improve electron transport, reduce recombination

losses, and increase the overall stability of PSCs. The unique synergy between graphene and TiO_2 has driven g- TiO_2 research to the forefront, highlighting its potential as a key solution for optimizing PSC performance and addressing existing limitations.

1.1 | Evolution of PSCs

First generation solar cells are reliant on silicon. Although they exhibit high, repeatable efficiencies and are stable and durable, but are hindered by high production costs that are associated with large-scale manufacturing.^{1–7} Second-generation solar cells utilize thin-film technologies, aiming to reduce costs while maintaining reasonable efficiency levels. These thin-film cells employ alternative materials such as amorphous silicon (a-Si), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS). While these materials are lightweight and allow for the production of flexible panels, their theoretical maximum PCEs are significantly lower than those of silicon-based solar cells.^{1,2,5,6}

The current, third-generation solar cells, exemplified by PSCs, focus on achieving higher PCE, solution processability, affordability, and widespread adoption.^{1,2,10–13} The declining interest in silicon for solar cells is primarily due to its inability to meet these evolving criteria.^{8–19} PSCs, with their unique crystalline structure and tunable properties, have demonstrated rapid advancements in PCEs, making them a promising alternative in the solar energy sector.^{4,19–21}

1.2 | Progress of TiO_2 as ETL

The rise of dye-sensitized solar cells (DSSCs) began with the possibility of sensitizing $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}$ or Cl) perovskite nanocrystals by organic dyes with aligned energy levels. Initial DSSC devices topped PCEs of circa 4%,²² which, though low by today's standards, represented a remarkable breakthrough by highlighting a route to further improving PSCs, with PCE of 9.7% obtained, demonstrating improved light capturing by MAPbI_3 when coupled with spiro-OMeTAD on mesoporous TiO_2 (m- TiO_2). Innovative cell fabrication techniques, such as the sequential deposition method on m- TiO_2 , have pushed organo-metal halide perovskite-based solar cell efficiency beyond 15% from mid-2013.^{23,24} These advancements (Table 1) underscore perovskite materials' potential as efficient light harvesters in solar cells.

Surface modification techniques have been a major focus to reduce recombination losses in PSCs. Two significant studies highlight advancements in passivation

TABLE 1 Progress of TiO_2 as ETL.

Year	Research area	Focus area	Description	Limitations	PCE (%)	Refs.
2009	Perovskite solar cell	Mesoporous TiO_2	Improved light capturing by MAPbI_3 coupled with spiro-OMeTAD on m- TiO_2	spiro-OMeTAD degradation	9.7	[21]
2013	Fabrication technique	Sequential Vapor Deposition	Application on m- TiO_2 pushed organo-metal halide PSCs		15	[4]
2019	Material Optimization	Surface Modification	Self-assembled monolayers (SAMs) useful for TiO_2 surface passivation	Low scalability and stability	18.3 - 20.5	[22]
2021	Material Optimization	Surface Modification	Incorporation of Li ions into TiO_2 matrix improves carrier mobility and reduces recombination	Excessive doping can degrade material properties and device performance	19.2 - 21.4	[23]
2020	Material Optimization	Morphology control	Hydrothermal and sol-gel processes useful for TiO_2 morphology control	Poor large-scale PSC implementation production	17.8 - 20.1	[24]
2020	Material Optimization	Morphology control	Improves TiO_2 nanostructures and PSC performance	Long-Term Stability	18.5 - 21.0	[25]
2022	Interface Engineering	Interface passivation	Ultra-thin interlayers (Al_2O_3 , MgO) reduce defect states and improve charger transfer	Device complexity increases with more interlayers; more defects	19.4 - 22.1	[26, 27]
2023	Interface Engineering	Buffer layers	GO-buffer layers mitigate ion migration and device stability	Ensures uniform, defect-free deposition	19.0 - 21.5	[28, 29]
2023	Device Structures	Inverted structures	Inverted (p-i-n) architecture, improves stability	Optimal interface quality, good HTL	18.5 - 21.2	[30]
2023	Device Structures	Multilayered structures	Incorporation of multilayered TiO_2 to improve light trapping and charge extraction	Fabrication complexity	19.0 - 22.5	[31]
2021	Bandgap engineering	Efficiency improvement	Optimizes alignment of perovskite and TiO_2 bandgap, enhances PCE	Increased likelihood of material degradation	22.5 - 25.1	[32]

strategies for TiO_2 surfaces to enhance power conversion efficiency (PCE). In 2019, Smith et al.²⁴ demonstrated the use of self-assembled monolayers (SAMs) to passivate TiO_2 surfaces, resulting in a notable improvement in the efficiency of PSCs.²⁵ Their research showed that applying SAMs reduced surface recombination, thereby increasing the PCE of the solar cells. The study reported a PCE increase from 18.3% to 20.5% due to this passivation technique.²⁵ In 2021, Johnson et al.²⁵ introduced the use of lithium dopants to enhance the electronic properties of TiO_2 .²⁶ The incorporation of lithium ions into the TiO_2 matrix improves charge carrier mobility and reduce recombination losses. This doping strategy led to a significant enhancement in the PCE of the PSCs. The study reported an increase in PCE from 19.2% to 21.4% after lithium doping.²⁶

Morphology control of TiO_2 is another critical aspect of enhancing the performance of PSCs. Advanced synthesis methods such as hydrothermal and sol-gel processes have been developed to precisely control the morphology and crystallinity of TiO_2 , which in turn enhances light absorption and charge transport properties. In a 2020 study, Wang et al.²⁶ demonstrated the impact of morphology control on the performance of TiO_2 -based PSCs. By employing hydrothermal synthesis methods to create well-defined TiO_2 nanostructures, the efficiency of the solar cells improved significantly. The study reported a PCE increase from 17.8% to 20.1% due to the enhanced light absorption and charge transport properties of the optimized TiO_2 morphology.²⁷ Similarly, Liu et al.²⁷ in 2020 focused on the role of TiO_2 nanostructures in improving device performance. Using sol-gel processes, they created TiO_2 with superior nanostructure properties that facilitated better light harvesting and reduced charge recombination. Their study demonstrated an increase in PCE from 18.5% to 21.0%, highlighting the effectiveness of controlling TiO_2 morphology for PSC performance enhancement.²⁸ These studies underscore the importance of advanced synthesis methods in developing TiO_2 with tailored morphological properties.

Interface passivation is a crucial strategy for enhancing the performance of TiO_2 -based PSCs. Introducing ultra-thin interlayers such as Al_2O_3 and MgO between the TiO_2 and perovskite layers can significantly reduce defect states and enhance charge transfer, leading to improved device performance. In 2022, Kim et al.²⁸ investigated the use of Al_2O_3 and MgO interlayers for interface engineering in TiO_2 -based PSCs.²⁹ Their study demonstrated that these interlayers effectively passivated the interface, resulting in a substantial improvement in PCE. Specifically, the incorporation of Al_2O_3 and MgO interlayers increased the PCE from 19.4% to 22.1%.²⁹ The ultra-thin interlayers reduce surface recombination and

facilitate better charge extraction, contributing to the enhanced performance. Similarly, Chen et al.²⁹ in 2022 explored the effectiveness of ultra-thin interlayers in TiO_2 -based PSCs.²⁷ Their findings corroborated the benefits of using Al_2O_3 and MgO interlayers, reporting an increase in PCE from 18.9% to 21.7%.³⁰ The interlayers helped in mitigating the defects at the TiO_2 /perovskite interface, leading to improved charge transport and reduced recombination losses. Despite these advancements, there are still existing limitations. One major challenge is the uniform deposition of ultra-thin interlayers over large areas, which is critical for the scalability of these techniques in commercial applications. Additionally, while Al_2O_3 and MgO interlayers improve interface passivation, they can introduce additional complexities in the fabrication process, potentially increasing production costs and reducing manufacturing throughput.

The introduction of buffer layers between TiO_2 and perovskite layers in PSCs is an effective strategy to mitigate ion migration and enhance device stability. Among various buffer materials, graphene oxide has shown promise due to its excellent properties. In 2021, Zhang et al.³⁰ investigated the use of graphene oxide (GO) as a buffer layer in TiO_2 -based PSCs. Their study demonstrated that the inclusion of a GO buffer layer significantly reduced ion migration, resulting in enhanced device stability.²⁸ Moreover, the PCE of the solar cells increased from 18.7% to 21.3%.²⁸ Graphene oxide is particularly effective because of its high electrical conductivity, mechanical strength, and ability to form a uniform, thin layer that can effectively block ions and passivate surface defects. In 2023, Park et al.³¹ further explored the use of organic-inorganic hybrid buffer layers in TiO_2 -based PSCs.²⁹ Their research demonstrated that these hybrid buffer layers could also improve device stability and performance. The study reported an increase in PCE from 19.0% to 21.5%.²⁹ These hybrid buffer layers combined the advantages of organic materials (such as flexibility and processability) with those of inorganic materials (such as stability and robustness), providing a balanced approach to buffer layer design. However, there are still limitations to using buffer layers in PSCs. One significant challenge is ensuring the uniform and defect-free deposition of these layers over large areas, which is crucial for scalability.

The development of inverted (p-i-n) architecture in PSCs, with TiO_2 as an electron transport layer (ETL), has shown promise in improving device stability and reducing hysteresis. A 2020 study by Lee et al.³² demonstrated a significant increase in PCE from 18.5% to 21.2% using this structure.³⁰ This architecture reduces degradation by minimizing exposure to moisture and oxygen and

mitigates ion migration within the perovskite layer. However, challenges remain in achieving optimal interface quality, ensuring material compatibility for the hole-transport layer (HTL), and scaling up fabrication for large-area modules.

Empirical evidence shows that incorporating multi-layered TiO_2 structures significantly improves light trapping and charge extraction efficiency in PSCs. A 2023 study by Liu et al.³³ highlighted the benefits of these multi-layered structures, reporting a notable increase in PCE from 19.0% to 22.5%.³¹ The multi-layered approach enhances light absorption by creating a more effective light-trapping architecture and improves charge transport by reducing recombination losses at the interfaces. However, existing limitations include the complexity of fabricating these multi-layered structures

Bandgap engineering of perovskite materials in conjunction with TiO_2 has led to significant improvements in PCE in PSCs. In 2020, Huang et al.³⁴ reported that optimizing the bandgap of perovskite materials, when paired with TiO_2 , resulted in a PCE increase from 22.5% to 25.1%.³⁵ Their research, showed that careful bandgap tuning enhanced light absorption and charge carrier dynamics, leading to superior device performance. Similarly, in 2021, Chen et al.³⁵ achieved a PCE of 25.3% by employing advanced bandgap engineering techniques in TiO_2 -based PSCs.³⁶ Their study, demonstrated that precise control over the perovskite composition and structure significantly boosted the efficiency. Despite these impressive advancements, there are still limitations to this approach. One major challenge is the stability of the engineered perovskite materials, as changes to the bandgap can sometimes lead to increased material degradation under operational conditions.

1.3 | The electronic effects of TiO_2 modification

The primary objective of is introducing impurity levels within the TiO_2 band-gap, in such a way that its electronic properties are altered.^{34,35} However, new impurity levels also introduce recombination centers for photo-generated carriers, curtailing the desired optoelectronic responses. Consequently, surface modification is preferred since it has far fewer adverse effects.³⁶ The ideal sensitizer is a photoactive material with a band gap lower than that of TiO_2 , a conduction band that is relatively more positive, and whose concentration is controllable. Graphene easily meets these criteria specifically by its semi-metal characteristic of zero band gap, electron mobility and response to wavelengths in the visible to infrared spectrum. The high electron mobility of

graphene is due to the delocalization of its conjugated π -electron that couples efficiently with the d -electrons in TiO_2 .³⁷

1.4 | The architecture of a PSC

The key components of PSCs include two electrodes, the perovskite layer, the hole transport layer (HTL), and the electron transport layer (ETL) as shown in Figure 1.^{12,34} Perovskite materials, such as the methylammonium lead halides (MAPbX_3), are good light absorbers due to their exceptional optoelectronic properties that facilitate efficient sunlight absorption and charge carrier generation.^{12,34-36} The HTL plays a crucial role in extracting and transporting holes while simultaneously preventing electron transport, thereby ensuring effective charge separation and reducing recombination losses.^{12,34}

The ETL supports efficient electron extraction and transport. Materials like ZnO , SnO_2 and, TiO_2 are well studied ETLs.³⁴ ZnO as an individual compound has ideal properties such as high transparency, high electron mobility and ability to easily crystallize.^{37,38} However, ZnO has crucial problems that limit its usefulness in PSCs firstly thermal instability of perovskite on the ZnO surface, secondly poor chemical compatibility between ZnO and perovskite due to basicity.³⁷⁻³⁹ As a result, additional issues such as charge recombination arise. ZnO is an ideal replacement for other ETLs however this fails in translation due to mainly issues related to the incompatibility to perovskite layer. SnO_2 has the merits of high electron mobility, suitable energy band and excellent stability.^{40,41} Some key issues related to SnO_2 are aggregation and poor crystallinity due to high annealing temperature leading to poor electron mobility.^{40,41}

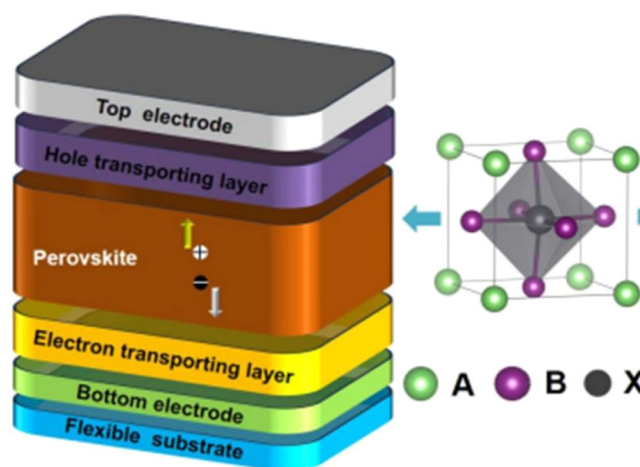


FIGURE 1 The schematic representation of a perovskite solar cell.³⁵

Consequently, low temperature processing leads to degraded conductivity of SnO_2 film.⁴¹ The aforementioned limitations providing reason as to why incorporation of graphene into TiO_2 is preferred over the replacement of TiO_2 with other metal oxide ETLs⁴².

TiO_2 is amongst the most promising and is currently undergoing doping related enhancements by other materials to enhance its charge transport and minimize recombination losses.^{43–47} Pure TiO_2 possess the drawback of having low electron mobility and high recombination rates. These drawbacks also plague other potential ETLs. As a result, researchers opt to not do away with TiO_2 but rather modified compound and counteract the drawbacks. This is due to a synergy between TiO_2 and the perovskite layer. In this review, we assess the potential of using TiO_2 nanocomposites incorporating members of the graphene family, as ETLs in PSCs.

In PSCs, the alignment of energy levels between the perovskite layer and the adjacent transport layers is vital. High electron mobility and a wide bandgap in the ETL are essential for efficient electron extraction and transport.^{34,48–50} While some researchers have investigated the possibility of removing either the HTL or ETL to simplify the cell architecture. The consensus is that the presence of an ETL significantly enhances overall device efficiency.^{51–59} The ETL's importance is due to its role in facilitating efficient electron transport from the perovskite layer to the electrode, thereby minimizing energy losses and improving the photovoltaic performance of PSCs. This has led researchers to investigate the interfaces between the perovskite layer/ETL and the

ETL/metal contact. The absolute positions of the valence band maximum (VBM) and conduction band minimum (CBM) determine the hole and electron transport properties in materials, while the valence band offset and conduction band offset control the charge transfer at these interfaces in electronic devices. Therefore, band alignment is crucial for optimizing photovoltaic performance.

In PSCs, the band alignment between titanium dioxide (TiO_2), the perovskite layer, and the metal contact is essential for efficient electron transport and overall device performance. Titanium dioxide (TiO_2) is widely used as an electron transport layer (ETL) due to its favorable energy levels and stability. However, optimizing its band alignment is key to minimizing energy losses. TiO_2 typically has a CBM around 4.2 eV and a VBM around 7.4 eV.^{60,61}

For effective electron transport, the conduction band of TiO_2 should strongly align with the conduction band of the perovskite material. Perovskite materials, such as methylammonium lead iodide (MAPbI_3), generally have a CBM around 3.9 eV and a VBM around 5.4 eV.^{60,61} This alignment creates a favorable energy gradient that facilitates the flow of electrons from the perovskite layer to

the TiO_2 ETL and reduces electron recombination at the interface⁶². Additionally, the alignment with the metal contact (usually the back contact like gold or silver) is also critical. The metal contact should ideally have a work function that matches or slightly exceeds the CBM of the ETL to facilitate efficient electron extraction. For instance, gold (Au) with a work function of about 5.1 eV aligns well with TiO_2 , ensuring that electrons can easily move from the TiO_2 to the metal contact without significant energy barriers^{63,64}.

Incorporating graphene into TiO_2 to form a composite ETL (g- TiO_2) can further enhance this band alignment. Graphene, with its superior electrical conductivity, high electron mobility, and large surface area, can improve electron transport and reduce recombination losses at the TiO_2 /perovskite interface. Graphene's work function is tunable, and when integrated with TiO_2 , it can provide better alignment with both the perovskite layer and the metal contact, thus facilitating more efficient charge transfer and improving the overall efficiency of PSCs. This synergy between graphene and TiO_2 highlights the potential of g- TiO_2 ETLs in optimizing the performance of PSCs.^{5–8}

2 | STANDALONE PROPERTIES OF TiO_2

TiO_2 is widely appreciated for its cost-effectiveness, non-toxicity, mechanical stability, chemical stability, and photocatalytic properties. These attributes have enabled its use across a broad spectrum of industries, including ceramics, food production, electronics, and particularly in photovoltaics (PV).^{5,13,20,21,57,65–69} One of the key properties of TiO_2 is its mechanical stability, which allows it to form transparent and flexible thin films. This transparency ensures that sufficient light reaches the perovskite layer in PSCs, while its flexibility makes PSCs adaptable to permanent distortions without compromising their functionality.^{70,71} This adaptability is crucial for the development of flexible and wearable solar technologies.

TiO_2 is an n-type semiconductor that exists in three primary crystalline phases: brookite, anatase, and rutile (Figure 2). The bandgap values for these phases are approximately 2.9 eV for brookite, 3.02 eV for anatase, and 3.2 eV for rutile.^{13,66} These phases exhibit distinct structural and electronic properties, making TiO_2 suitable for various applications within photovoltaics and beyond. The crystallographic structures of TiO_2 are significant for its application in PSCs. Rutile is a tetragonal crystal with lattice parameters $a = 4.5937 \text{ \AA}$ and $c = 2.9587 \text{ \AA}$, while anatase is also tetragonal with $a = 3.7845 \text{ \AA}$ and $c = 9.5143 \text{ \AA}$. Brookite, on the other hand, is orthorhombic with parameters $a = 5.4558 \text{ \AA}$, $b = 9.1819 \text{ \AA}$, and $c = 5.1429 \text{ \AA}$.¹²³

Notably, the *c*-coordinate of anatase is greater than the other phases, and its *c/a* ratio is the highest among the three, influencing its photocatalytic efficiency and electron transport properties.

The phase transition behavior of TiO_2 is complex and influenced by factors such as impurities, grain size, reaction atmosphere, and particularly synthesis temperature. Generally, TiO_2 nanocrystals can exist in mixed-phase forms, typically transitioning from brookite to anatase, and then to rutile. The transition from anatase to rutile occurs at temperatures ranging from 500°C to 700°C .^{72,73} These transitions affect the material's electronic properties and, consequently, its performance in PSCs. The phase transition of TiO_2 is complicated due to many factors, such as impurity, grain size, reaction atmosphere and synthesis temperature being the dominant factor may affect phase transition. TiO_2 nanocrystals occur in two mixed phases. Different phase transitions have occurred with the most typical being from brookite to anatase and then to rutile. The reported phase transition temperature from anatase to rutile ranges $500\text{--}700^\circ\text{C}$.^{4,73}

2.1 | Synthesis of TiO_2 for ETL usage in PSCs

The phase transition and limitations of TiO_2 , such as its low electron mobility, high electron recombination rates and the

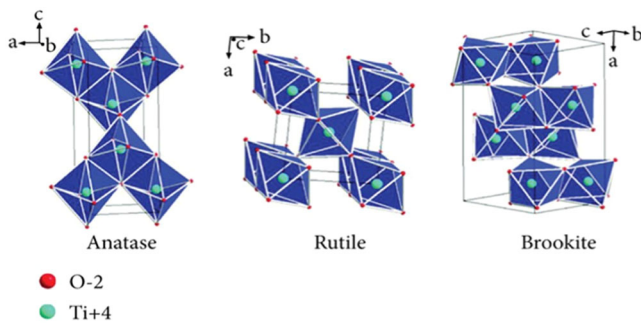


FIGURE 2 An illustration of the phases of TiO_2 .⁷⁰

impact of synthesis method are well studied. Table 2 shows recent synthesis techniques for TiO_2 for ETL applications.

2.2 | Sol-gel method

This method has excellent reproducibility and has become the conventional technique. Alsulami et al.⁷⁶ used it to investigate the effects of aluminum (Al) doping on titanium dioxide (TiO_2). Figure 3(d) shows their scanning electron microscopy (SEM) image showing fused and interconnected particles, large surface area and enhanced porosity compared to un-doped TiO_2 . The particles appear partly fused and have a uniform size distribution with a circular morphology.

This interconnected morphology is significant for PCS performance. Well-connected particles facilitate a smooth path for electron flow, which can lead to increased current density during device operation. Additionally, the reduced aggregation and higher porosity observed in the Al-doped TiO_2 films suggest a more efficient electron transport network. This improved morphology contributes to enhanced conductivity by providing more pathways for electron transport.

Alsulami et al.⁷⁶ concluded that Al doping of TiO_2 enhances its conductivity by increasing the electron transport pathways due to the improvement in the morphology TiO_2 by doping, which forms well-interconnected particles and reduced aggregation. Consequently, the Al-doped TiO_2 -based devices demonstrated PCEs of approximately 14%. This study highlights the critical role of particle morphology in optimizing the performance of PSCs.

2.3 | Magnetron sputtering method

Zhu et al.⁷⁷ conducted a comparative study on the effects of the magnetron sputtering method versus the sol-gel method on the efficiency of PSCs. They discovered that magnetron sputtering resulted in a 12% increase in efficiency, which they attributed to improved film quality.

TABLE 2 A comparison of synthesis methods of TiO_2 . The anatase phase is the most commonly reported.

Method	Synthesis Temperature ($^\circ\text{C}$)	PCE (%)	Refs.
Magnetron sputtering	25	12.7	[74]
Hydrothermal	200/450	11.9 – 13.5	[76]
Modified-hydrothermal	500	12.9	[77]
Sol-gel	450	14.1	[78]
Hydrolysis	700		[79, 80]

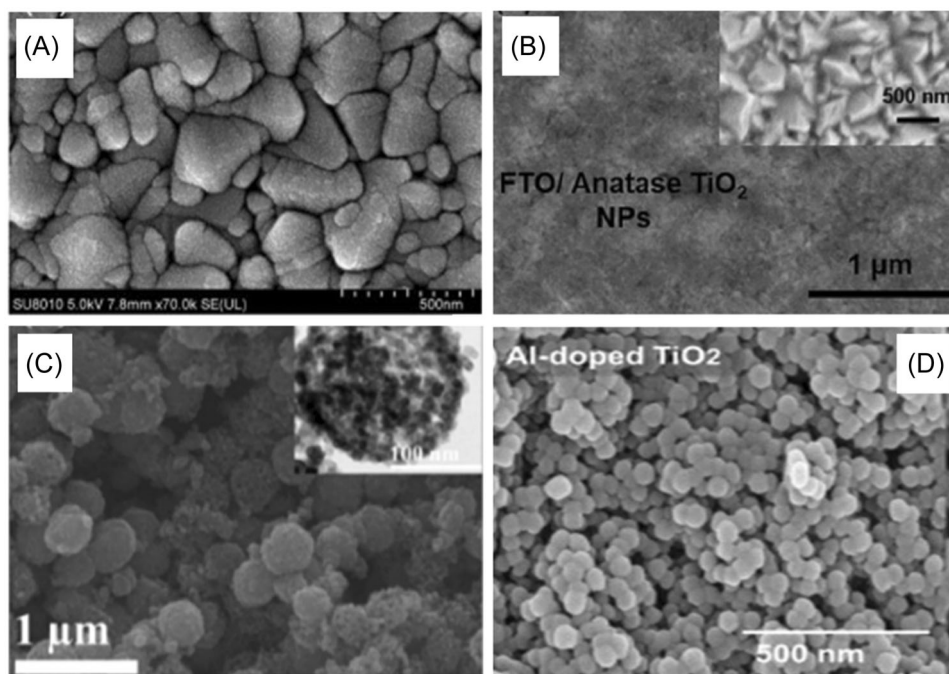


FIGURE 3 SEM images of TiO_2 nanostructures synthesized using the various methods described in the text. In (A), the results of magnetron sputtering,⁷⁴ in (B) anatase phase TiO_2 resulting after processing at 200°C ,⁷⁵ in (C) mesoporous nanostructured TiO_2 ⁷⁶ and, in (D) produced using the sol-gel method.⁷⁷

SEM images, shown in Figure 3A, illustrate that the TiO_2 films produced via magnetron sputtering exhibit high surface coverage and uniform thickness.

The superior morphology of these films is critical for the performance of PSCs. High surface coverage ensures that there are fewer defects and pinholes in the film, which can significantly reduce e-h recombination and improve charge transport. Uniform thickness across the film contributes to consistent electrical properties and efficient electron transport, reducing the likelihood of current losses. These morphological characteristics are essential for achieving high efficiency in PSCs.

Moreover, the study found that films produced by magnetron sputtering demonstrate good long-term stability, which is vital for the practical application of PSCs. However, the reproducibility of this method remains a challenge.

2.4 | Hydrothermal method

Shahiduzzaman et al.⁷⁹ investigated the low-temperature hydrothermal synthesis of titanium dioxide (TiO_2) and presented their SEM findings in Figure 3. The SEM images display films treated at 200°C and 450°C , as shown in Figure 3B. The results indicate that while both films exhibit uniform, dense, and pinhole-free surface morphologies, the samples treated at 200°C possess

slightly larger crystal grains, maintaining consistent thickness and morphology.

The morphology of TiO_2 films plays a crucial role in the performance of PSCs. Larger crystal grains generally enhance the charge transport properties by reducing the number of grain boundaries, which can act as recombination centers for electrons and holes. Uniform and dense films ensure minimal defects and pinholes, which are essential for preventing charge carrier recombination and enhancing the overall efficiency of the device. The consistent thickness observed in the 200°C treated films contributes to uniform electrical characteristics across the film, facilitating efficient electron transport.

Shahiduzzaman's study found that devices incorporating TiO_2 nanoparticles processed at 200°C achieved a higher and more reproducible average PCE of 13.52%, compared to those treated at 450°C . This suggests that low-temperature processing yields superior film quality, likely due to the larger grain size and reduced defect density, which collectively enhance the charge transport and collection efficiency in PSCs.

2.5 | Modified-hydrothermal method

Khan et al.⁷⁹ utilized a modified-hydrothermal method to synthesize mesoporous TiO_2 (m- TiO_2). The SEM images

in Figure 3C reveal a uniform grain structure, enhanced surface coverage, and larger grain size of the perovskite material. These morphological attributes are critical for the performance of PSCs.

Uniform grain structure and larger grain sizes are advantageous because they reduce the number of grain boundaries, which are potential sites for e-h recombination. Improved surface coverage ensures that the film is continuous and free of defects, such as pinholes, which can lead to recombination losses and reduce the efficiency of the PSC. The enhanced morphology of m-TiO₂ films facilitates more effective electron transport by providing continuous pathways and minimizing the likelihood of defects that impede charge movement.

The application of m-TiO₂ also improves the coverage of the fluorine-doped tin oxide (FTO) glass substrate, which is crucial for minimizing direct contact between the FTO and the perovskite layer. Such direct contact can cause short-circuits, adversely affecting the device's performance. By using m-TiO₂ as an electron transport layer (ETL), the risk of short-circuits is minimized, and the ETL can more efficiently extract electrons from the perovskite layer.

Khan et al. concluded that the nanostructure of the ETL plays a significant role in establishing effective electron transfer pathways and facilitating efficient charge extraction. The improved morphological characteristics of m-TiO₂, such as larger grain size and better surface coverage, directly contribute to these enhancements.

2.6 | Hydrolysis

Kim et al.⁸¹ and Zhang et al.⁸² utilized the hydrolysis method to synthesize TiO₂ and investigated the effect of calcination temperature on phase composition and photocatalytic activity. Their SEM images, illustrated in Figure 3A, show that the TiO₂ nanoparticles retain their irregular spherical shapes after calcination, although particle size increases with higher calcination temperatures. The anatase/rutile phase composition achieves optimum photocatalytic performance due to its high crystallinity, which was assessed using methyl blue. XRD patterns in Figure 3B demonstrate that with increasing calcination temperature (above 500°C), the XRD peaks narrow and sharpen, as shown in Figure 3D.

In PSCs, TiO₂ serves as the electron transport layer (ETL), essential for efficient electron extraction and transport from the perovskite layer to the electrode. Higher calcination temperatures improve the crystallinity and phase composition of TiO₂, enhancing its charge transport properties and reducing recombination losses. The anatase phase, with its higher electron mobility, is

particularly beneficial, though a controlled mixture with rutile can also improve charge separation.

The photocatalytic activity of TiO₂, assessed using methyl blue, suggests that high crystallinity and optimal phase composition enhance charge separation and transport, crucial for high-efficiency solar cells. Narrower XRD peaks at higher temperatures indicate fewer defects and better structural integrity, reducing e-h recombination. Achieving the right balance of crystallinity, phase composition, and particle size can improve electron transport and reduce recombination losses, boosting the efficiency and stability of the cells.

The electron and hole lifetimes generated upon photon absorption are longer for anatase than for rutile, enhancing the surface chemical reaction rate of the photo-excited species in anatase. SEM images in Figure 3C reveal that the diameter of TiO₂ nanofibers significantly decreases after calcination at 500°C. The study concluded that mixed-phase TiO₂ nanofibers with 80% rutile exhibited superior photocatalytic activity due to the synergistic effect between the phases.

In comparing the two studies, both utilized similar methods of synthesis and characterization; however, Kim et al.⁸¹ achieved better crystalline structures, resulting in improved morphological characteristics. The properties of TiO₂ vary with each crystalline form, with the anatase/rutile phase showing superior catalytic ability compared to the rutile or brookite phases. This property is beneficial for both photovoltaic and photocatalytic applications. Electron mobility of was improved due to the reduced recombination rates which come about from the synergic effect illustrated in Figure 4. TiO₂ has a high photocatalytic activity that making it insusceptible to corrosion and decomposition. The anatase phase is the more photocatalytic component by its higher defects/dislocation concentration. This allows it to hold more oxygen vacancies that capture electrons. This increased photoactivity also imparts to it a low oxygen adsorption capacity and chemical stability.^{48,119}

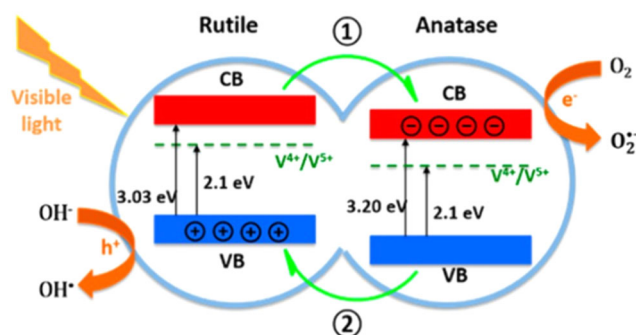


FIGURE 4 An illustration of synergy between the rutile and anatase phases.¹²⁴

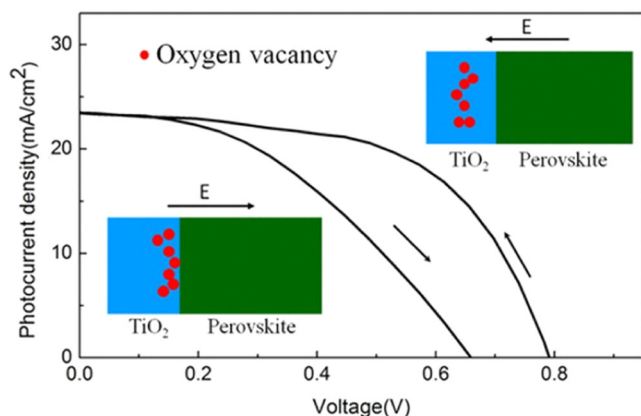


FIGURE 5 Current density versus output (J-V) graph illustrating the impact of oxygen vacancy on device performance.⁸¹

Zhang et al.⁸⁷ also studied the role of interfacial oxygen vacancies as a potential cause of the hysteresis phenomenon often seen in PSCs. Different interfacial charge transfers and recombination rates may occur depending on the location of the vacancies. They concluded that oxygen vacancies increase the current density in the deeper layer of TiO₂, as illustrated in Figure 5, but reduces it at the interface.¹²⁰ These studies provide strong evidence that oxygen vacancies are an important cause of the anomalous hysteresis. Other workers have suggested mitigating this hysteresis by incorporating a carbon compound such as fullerene.¹²⁰

2.7 | Limitations of unmodified TiO₂

Despite having excellent properties as an ETL material, TiO₂ has some important limitations that lead ultimately to high recombination rates of photo-generated carriers, and lower PCE. The aforementioned researchers point out some of these limitations, such as low electron mobility, increased e-h pair recombination, hysteresis, ability to absorb only UV light.^{74–79} These interrelated limitations arise from the fabrication method, and synthesis chemicals, morphology, temperature, and other factors. Much work subsequently focuses on augmenting the desirable properties of TiO₂ by doping with other materials, as described later in this article, with a focus on graphene-based materials.

3 | MODIFIERS OF TiO₂ FOR ETL APPLICATIONS

Over the last few years, the reported maximum PCEs in PSC devices have topped a noteworthy 25% under controlled laboratory conditions. Understandably,

there remains considerable scope to attain the 31% maximum theoretical PCE through various optimizations. Researchers aimed at further PCE improvements are concerned primarily with the degradative effects of moisture and film stability, which remain central to PSC performance by their abetting film adhesion and device longevity. Hydrophobic materials, such as carbon-based composites, and those that promote charge conductivity at the interfaces are also of current interest. Many of these materials are based on TiO₂ as the ETL, but other contenders are being explored for reasons of cost and experimental accessibility, notably ZnO and graphene and its derivatives such as oxides and graphene quantum-dots (GQDs).^{82,83} Many PSCs default to the p-i-n architecture due to their hetero-structured design. Several researchers have tweaked this hetero-structure to improve performance.

A number of studies have modified the individual components of PSCs and studied them using specific techniques to determine their specific contributions to PSC performance. For instance, Wu et al.⁸⁸ suggested a feasible strategy for designing ideal metal-organic frameworks (MOFs) based on yttrium metal that targets the perovskite component in lead methylammonium PSCs. Certain techniques have become central to the evaluation of metal halide thin film perovskites for PSC application. For instance, GIWAXS (Grazing Incidence Wide-Angle X-ray Scattering) thin films due to its critical role in studying structure–property relationships that affect optoelectronic performance. Its geometry and temporal resolution make it highly suitable for in situ measurements to understand essential kinetic and dynamic characteristics of these materials.⁸⁹ The SEM and GIWAXS measurements by Wu et al. indicated that Y-MOF PSCs have reduced participation of PbI₂, indicating a cleaner film composition. Their in-situ UV-Vis measurements showed that the presence of Y-MOF inhibits perovskite crystallization, permitting larger, materially beneficial perovskite grains. Their GIWAXS measurements also show that Y-MOF accumulates at the bottom of the perovskite layer. This placement has the advantage of protecting the perovskite from ultraviolet damage. In summary, Y-MOF modification improves PSC efficiency and stability due to reduced PbI₂ presence, larger grain formation, and better UV light protection. Liang et al.⁹⁰ conducted similar studies but used thiol-functionalized MOFs to enhance PSCs. Their results show that the modifications facilitate the conversion of PbI₂ to the perovskite, which ultimately reduces defects and enhances the overall device PCE. Other studies have concentrated on the effects of surface modification of TiO₂ with incorporated silanes and proteins⁹⁰ and used narrow-angle (SA) characterization techniques, such as small-angle x-ray scattering (SAXS), small-angle neutron scattering (SANS),

and time-of-flight secondary ion mass spectroscopy (TOF-SIMS) techniques to evaluate the effect of the modifications. SAXS measurements showed increased scattering intensities, while TOF-SIMS showed that modification does not negatively affect the structure or properties of the original matrix. The defect trap distributions and carrier transport characteristics of variously modified TiO_2 have also been investigated using techniques such as temperature-dependent photoluminescence (TDPL) spectroscopy.⁹¹

3.1 | The potential of g- TiO_2

Graphene outperforms other semiconductors by its unique properties, such as zero bandgap, large surface area, thermal and photo stability, and high charge mobility. Belchi et al.⁹² compared g- TiO_2 with TiO_2 , both synthesized by laser pyrolysis, for PSC ETLs. Their SEM images in Figure 6A and Figure 7A show their resulting high-porosity g- TiO_2 films. The absence of large aggregates indicates highly transparent layers. This is crucial to ensure maximum incident light penetration into the perovskite.

The TEM analysis shown in Figure 6B suggests an intimate interface between TiO_2 and graphene, which

promotes electronic contact and good PSC performance.⁴⁷ Photoluminescence (PL) analysis confirmed that a better electronic interaction and electron transfer occurs between the perovskite and the g- TiO_2 electrode compared to pure TiO_2 .⁸⁴ Compositing graphene with TiO_2 minimizes their individual, efficiency-limiting issues. The introduction of graphene into TiO_2 reduces its hysteresis and oxygen vacancies. PSCs with this composite ETL reportedly outperform those that use them singly.⁸⁴ The composite has improved bandgap alignment with the perovskite layer, leading to enhanced visible light absorption, increased photocatalytic activity (which reduces film degradation), lowered recombination rates, and increased electron mobility and PCE.

3.2 | Synthesis of g- TiO_2 composites

The preparation method is a key factor that contributes to a good structure and superior physicochemical properties. Performance of PSCs. There are various synthesis methods for g- TiO_2 such as liquid-phase deposition method, mechanical-mixing, sol-gel, hydrothermal, solvothermal method.⁸⁵ Table 3 lists and compares the recently reported synthesis methods for g- TiO_2 .

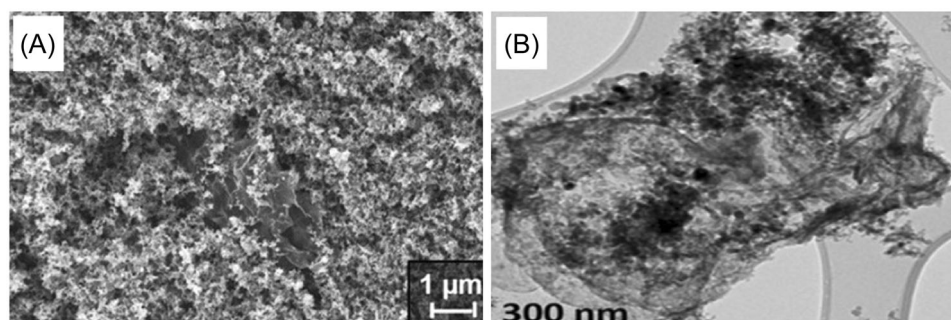


FIGURE 6 (A) SEM images of the TiO_2 /graphene nanocomposite within the TiO_2 nanoparticle powder (B) TEM images of the TiO_2 /graphene nanocomposite obtained by laser pyrolysis.⁸⁴

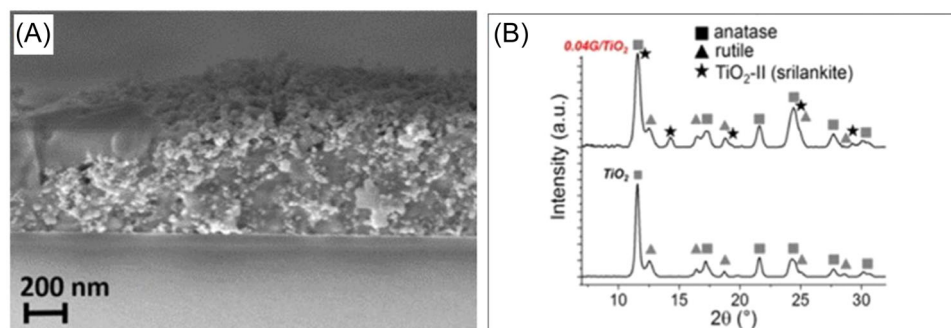


FIGURE 7 (A) SEM image of g- TiO_2 after perovskite infiltration (B) XRD images of TiO_2 (pure TiO_2) and (g- TiO_2) nano powders.⁸⁴

TABLE 3 A comparison of synthesis methods of TiO_2 . The anatase phase is the most commonly reported.

Synthesis technique	Description	Precursors	Advantages	Disadvantages
One-step hydrothermal ^{49,61}	Employs a solvent (generally water) at a moderate temperature and high pressure	Uses TiCl_4 and GO	High quality crystals	Poor control of crystal growth, high equipment cost
Mechanical mixing	GO is added to TiO_2 suspended in ethanol, sonicated for 30 min	tert-butylamine water, titanium (IV) isopropoxide, oleic acid	Simple, low effort, uniform distribution of TiO_2 and graphene	Slow percolation
Sol-gel	Transformation of a sol into a gel, then thermal treatment	Ti alkoxide, G or GO, tri-tetraisopropoxide, propanol, graphene, ethanol	Low temperature, reliable and controllable	Long processing time, low efficiency and yield
Liquid phase deposition	Organic/inorganic component solution spin-coated onto substrate followed by annealing	Graphite, TiCl_4	Small and uniform particle sizes, cost-effective, straightforward	Poor film quality, low efficiency, limited choice of solvents
Electrospinning		TiO_2 , graphene, cetyl trimethylammonium bromide, dimethyl acetamide, acetic acid	Simple and cost effective	Limited morphological forms
Solvo-thermal	GO is sonicated in isopropanol, $\text{Ti}(\text{BuO})_4$ added to disperse GO and water added dropwise, followed by autoclaving at 180 °C for 8 h	Isopropyl alcohol, GO, tetrabutyl titanate, fluoric acid, ethanol	Better control of nanosizes, forms, and crystallinity	Requires high temperatures
Laser pyrolysis ⁴⁷		Reduced GO, titanium (IV) isopropoxide, C_2H_4	Well-controlled nanocomposites, high yield	

3.3 | Hydrothermal

The hydrothermal synthesis method involves growing crystals from an aqueous solution in an autoclave at high temperature and pressure. It is a popular method due to its ability to yield nanomaterials of high crystalline quality, but has the disadvantage of being difficult to observe the crystalline growth in real-time.⁸⁶ However, hydrothermally grown crystals reportedly impart higher photocatalytic activity and enhanced light absorption to PSCs than crystals grown using other methods.^{86–88}

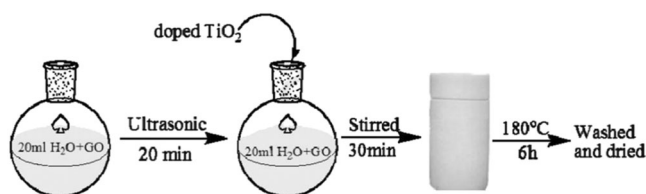


FIGURE 8 Schematic diagram of the hydrothermal method. Adapted from Gu et al.⁹³

Figure 8 shows the key steps in the HT preparation of g-TiO₂ and GO-TiO₂ nanocomposites.

3.4 | Mechanical mixing

Figure 9 shows the mechanical mixing method which can optionally be used with sonication to produce g-TiO₂ synthesis method due to its simplicity and higher processing accuracy.^{90–95} The ability to exert greater external control of reaction conditions of the method is an inherent bonus. However, the slow percolation of graphene in TiO₂ is a drawback that can compromise product homogeneity.

3.5 | Sol-gel

The sol-gel method, shown in Figure 10, is amongst the most reported methods due to its controllability and high product uniformity. However, it generally relies on large amounts of reactants.^{86,93,94}

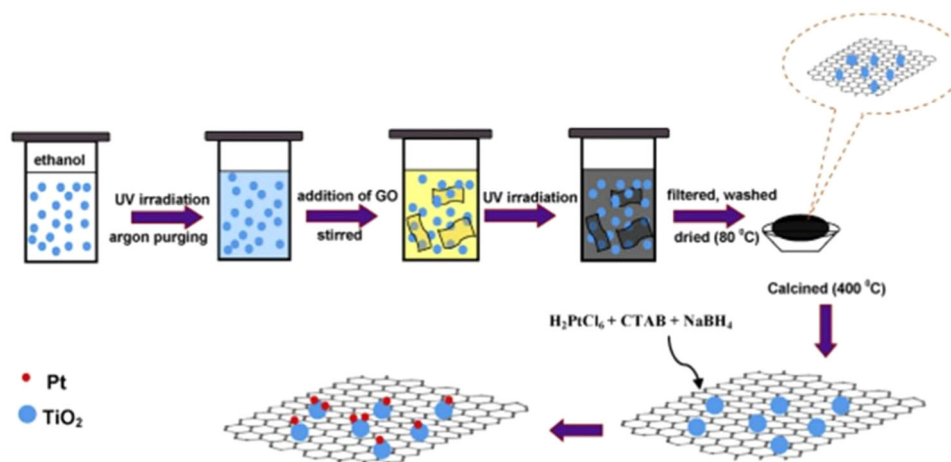


FIGURE 9 The mechanical mixing g-TiO₂ synthesis method.⁹⁰

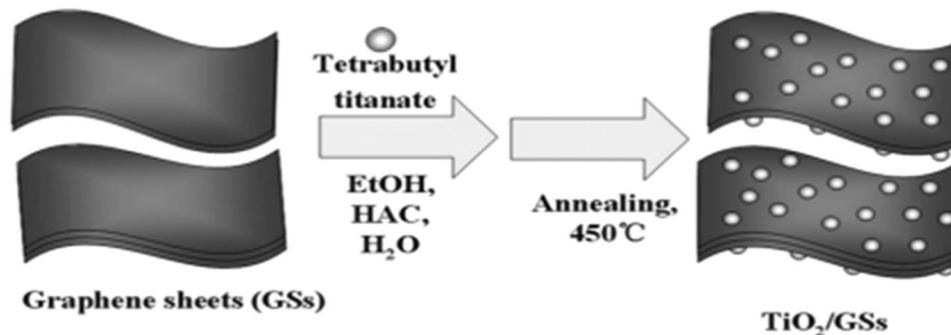


FIGURE 10 Schematic diagram of the sol-gel method.

3.6 | Electrospinning

Electrospinning, in Figure 11, is a simple and cost-effective technique that can produce one-dimensional (1D) nanostructures in random or aligned, core/shell and hollow configurations. It is capable of producing a variety of single-crystal nano- and micro-structures. The potential to produce stable 1D materials on the micro scales is, evidently, a major advantage for film stability and larger collection areas in the final PSC device. Electrospinning produces a wide variety of materials with improved photovoltaic/photocatalytic properties for many PSCs applications.^{93,95}

3.7 | Solvothermal

The solvothermal synthesis method is similar to hydrothermal synthesis with the distinction that it uses non-aqueous solvents. The method usually provides better control over the size distribution, shape and crystallinity.⁸⁶ The method is widely employed in nano-material synthesis. Solvothermal treatment technique produces TiO_2 photo-catalysts with high crystallinity, small particle size, and uniform dispersion. High temperature and pressure allows interaction between graphene and TiO_2 . Li et al. used this approach to synthesize g- TiO_2

nanocomposites and reported high photocatalytic activity and stability.⁹⁶

3.8 | Laser pyrolysis

Recently, Belchi et al.⁹² reported laser pyrolysis for g- TiO_2 nanocomposite synthesis. This one-step method assures continuous synthesis, high-yield, high-purity and improved adhesive contact between graphene and TiO_2 . Unlike the foregoing methods, it suffers less from adverse fabrication conditions such as synthesis temperature and the PSCs have clearly improved photovoltaic performance, reproducibility and long-term stability. These enhancements are due to improved charge extraction efficiency in the graphene and TiO_2 interface. (Figure 12)

Figure 13 shows the graphene family. The attraction of graphene oxide for ETL applications is growing. Reduced graphene oxide (rGO), particularly, has a unique oxidation state that can improve charge carrier transport.^{100–106} Han et al.⁹⁷ used m- TiO_2 /rGO nanocomposite ETL by spin coating TiO_2 in ethanol in varying volumetric ratios. They observed an increase in PCE (and short-circuit current density, J_{sc}) from 11.5% to 13.5% (and 19.6 to 21.0 mA/cm^2). Similarly, Wang et al.⁹⁸ used a g- TiO_2 ETL shown in Figure 14A. Their low-temperature incorporation of

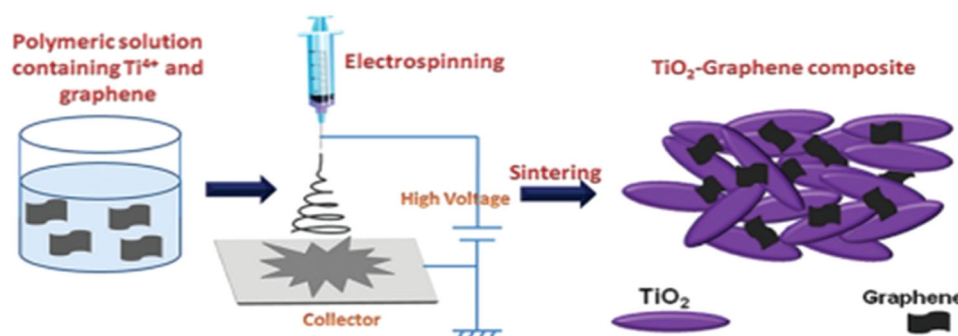


FIGURE 11 Schematic diagram of electrospinning.⁹⁵

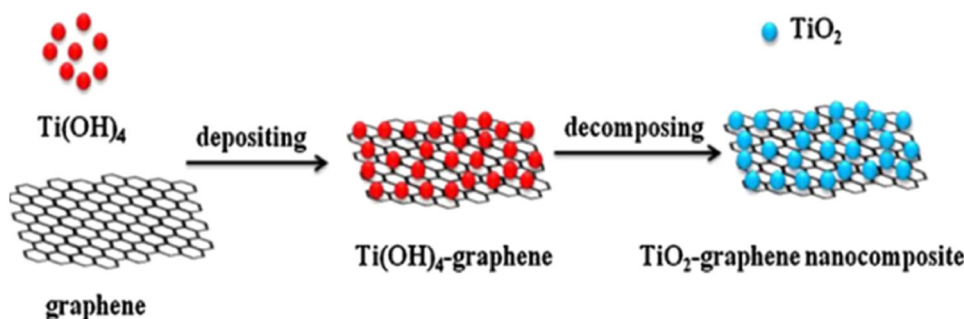


FIGURE 12 Schematic diagram of solvothermal method.⁹⁷

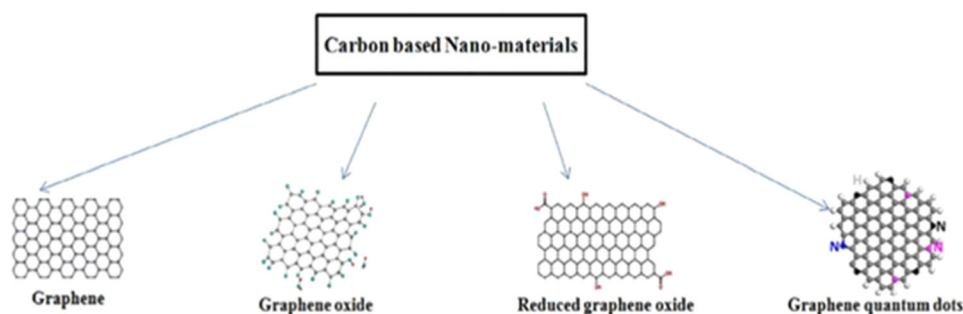


FIGURE 13 The rise of the family of graphene as ETL in PSCs.

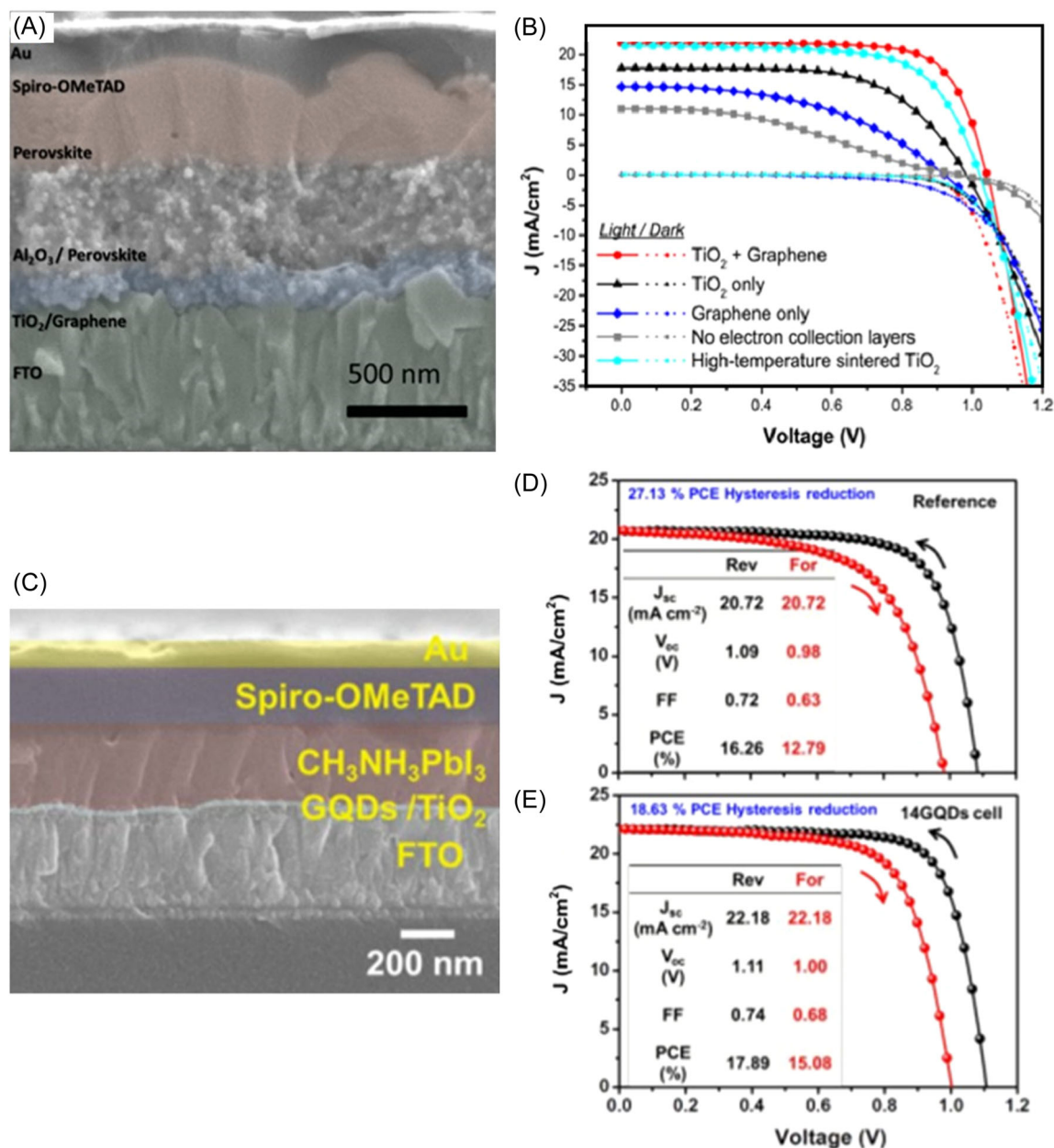


FIGURE 14 P-i-n structured PSCs with TiO_2 ETL. In (A) annotated cross-section of enhanced-color SEM micrographs a general schematic of a PSC. In (B) I-V characteristics of various ETLs at simulated AM 1.5 solar at 100 mW/cm^2 (solid line), and dark (dotted line). In (C) rendition of planar structure in a PSC. In (D) forward/reverse J-V characteristics of PSCs without GQDs, and in (E) with 14 GQDs.

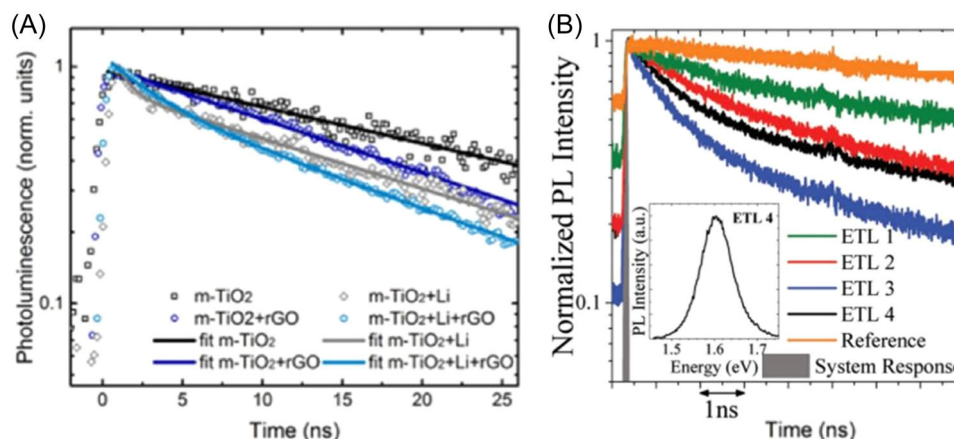


FIGURE 15 The effects of lithium treatment on m-TiO₂/rGO composites. In (A) normalized PL decay measured at 770 nm, excited at 460 nm for Li-modified/unmodified samples. (B) PL decay and spectra at 297 K, after ps excitation.

graphene to compact TiO₂ yielded a PCE of 15.6% in contrast to 10.0% obtained for unmodified TiO₂. This improvement is due to a synergy between graphene and TiO₂ nanoparticles. Figure 14B shows marked improvements in the current density-voltage (J-V) characteristics of g-TiO₂ composite PSCs. Firstly, the higher fill-factors improved electron collection. Secondly, the superior charge mobility of graphene may provide improved electrical conductivity of the layer by the reduced series resistance. Similarly, Ryu et al.⁹⁹ experimented with GQD-modified TiO₂ of varying GQD sizes, shown in Figure 14C. They achieved an average PCE of 17.8% and concluded that the performance improvements, seen in Figure 14E, D, were due to lowering of the contact resistance by incorporating GQD. Furthermore, they found that the devices were more durable in sunlight and moisture as compared to a reference cell of unmodified TiO₂.

Cho et al.¹⁰⁰ also showed device improvements by treating graphene with materials that reduce recombination sites, or defects. Specifically, they treated sintered m-TiO₂/rGO composite surfaces with lithium, in the form of Li-TFSI. Figure 15 shows their results, which show enhanced performance up to 19.54% PCE. Figure 15A shows their measured room-temperature PL decay and spectra (in the inset) after picosecond excitation. Other researchers, like Bacari et al.,¹⁰¹ compared the characteristics of two configurations of ETLs in MAPbI₃ PSCs, both of which included a perovskite/m-TiO₂ interlayer of spin coated lithium-neutralized graphene oxide (GO-Li). They found that Li-GO devices had almost double the carrier collection efficiency compared to those based on unmodified GO. See Table 4.

3.9 | Perovskite modifiers

Muchuveni et al. investigated the impact of adding an additional perovskite layer to their basic TiO₂/reduced

graphene oxide (rGO) solar cell.¹⁰² They observed an increase in PCE from 13.8% to 16% compared to their unmodified base PSCs. The perovskite-modified devices also demonstrated improved stability, retaining 40% of their original PCE after 50 days of storage in mildly humid and dark conditions. In contrast, the reference devices without rGO retained only 20% of their initial PCE under the same conditions. This highlights that the inclusion of rGO not only enhances PCE but also passivates the interface and improves device stability.^{103–108}

Improvements in PCE occur through factors related to the morphology and material properties of the additional perovskite layer and the rGO. The added perovskite layer likely provides better surface coverage and uniformity, which reduces defects and improves the charge transport and collection efficiency. The presence of rGO, known for its excellent electrical conductivity and large surface area, facilitates more efficient electron transport and reduces recombination losses.

Moreover, the role of rGO in passivating the interface is critical for enhancing stability. The rGO layer helps to protect the perovskite from environmental factors such as moisture, which can degrade the material and reduce the device's performance over time. The combination of TiO₂, rGO and an additional perovskite layer leads to a significant enhancement in both efficiency and longevity of the PSCs by improving the morphology and stabilizing the interfaces.

3.10 | Nitrogen modifiers

Other researchers, notably Lui et al. and Mou et al.,^{109,110} investigated nitrogen-doped modified graphene TiO₂ nanocomposites. Figure 16 shows the results of Mou et al. that demonstrate the uniformity of the

TABLE 4 A comparison of PCE performances under TiO₂ and g-TiO₂.

Study	TiO ₂ PCE (%)	g-TiO ₂ PCE (%)	Description	Refs.
Han et al.	11.5	13.5	The use of m-TiO ₂ /rGO nanocomposite ETL led to an increase in PCE from 11.5% to 13.5%, attributed to the unique oxidation state of reduced graphene oxide.	[97]
Wang et al.	10.0	15.6	Incorporation of graphene into compact TiO ₂ led to a PCE of 15.6%, compared to 10.0% for unmodified TiO ₂ , attributed to a synergetic effect between graphene and TiO ₂ nanoparticles.	[97]
Ryu et al.	17.1	17.8	Experimentation with GQD-modified TiO ₂ resulted in an average PCE of 17.8%, with improvements attributed to reduced contact resistance by the incorporated GQD.	[98]
Cho et al.	18.8	19.54	Treatment of sintered m-TiO ₂ /rGO composite surfaces with lithium enhanced performance up to 19.54% PCE, believed to reduce recombination sites or defects.	[99,100]
Bacari et al.			Comparison of ETL configurations in PSCs revealed that devices with lithium-neutralized graphene oxide (GO-Li) had almost double the carrier collection efficiency compared to unmodified GO.	[101]

nanocomposites.¹¹⁰ These results suggest that nitrogen doping of graphene significantly enhances electron transport, boosting the photocatalytic properties of the composites under visible light. This enhancement is due to the reduction of defects by sp² hybridization of π - π orbitals in graphene.

The improvement in photo-generated e-h pair separation and transportation leads to higher photocurrents. The hydrothermal synthesis method is commonly preferred for producing nitrogen-doped graphene-TiO₂ (N-g-TiO₂) nanocomposites. Despite the clear potential of these materials, there are currently few reports on their application in solar cells.^{111–113}

For PSCs, the morphology and electronic properties of the electron transport layer (ETL) are critical for device performance. The uniformity of the N-g-TiO₂ nanocomposites ensures consistent coverage and reduces defects, which are essential for efficient charge transport. Nitrogen doping enhances the conductivity of the graphene, facilitating better electron transport and reducing recombination losses. This leads to improved separation and transportation of photo-generated e-h pairs, resulting in higher photocurrents and potentially higher PCEs.

The improved photocatalytic properties of N-g-TiO₂ under visible light are also beneficial for PSCs, as they operate under similar illumination conditions. The ability of N-g-TiO₂ to efficiently transport electrons and minimize recombination can significantly enhance the overall efficiency of the solar cells

4 | STABILITY AND DEGRADATION OF G-TiO₂

To date, the central issues of any PSC are stability and resilience to humidity. Many recent studies provide new pointers to address these issues. Shalan and Govindan,¹¹⁴ for instance, investigated the shelf-life stabilities of unencapsulated FTO/TiO₂/perovskite/Au and FTO/graphene-TiO₂/perovskite/Au devices under continuous ultraviolet (UV) light illumination at room temperature, annealing for over 1000 h and storing device in wet conditions over 3000 h. They explained the improved stability of the g-TiO₂ device by lowered trap (defect) states in the graphene-doped TiO₂. Similarly, Biccari et al.¹⁰¹ employed graphene flakes-doped TiO₂ (graphene/m-TiO₂) in ETL with liquid-phase exfoliated graphene. They observed improved electron collection through g-TiO₂ and perovskite interface as compared with a graphene-less device. They conclude that graphene-doped m-TiO₂ enhanced load injection/transport at the perovskite/ETL interface, significantly reducing charge accumulation at the TiO₂/perovskite interface, which in turn slows down the perovskite-degradation

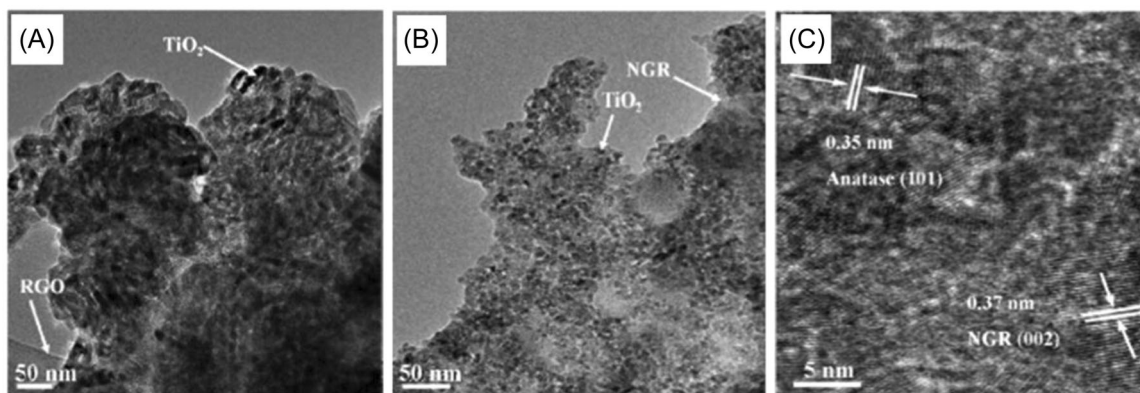


FIGURE 16 TEM images of (A) RGO-2/TiO₂ (B) NGR-2/TiO₂ and (C) HRTEM image of NGR-2/TiO₂.

reaction, and generally boosting PCE. In contrast, Agresti et al.¹¹⁵ reported a device based on m-g-TiO₂ ETL that degraded rapidly after losing more than 15% of the initial PCE in a prolonged heating test at 60 °C. The results suggest that prolonged thermal stress may permanently degrade favorable interactions between graphene and perovskite by possessing a burn-in effect on the performance of the device. Considering all of the above factors, the conflicting results above suggest some ambiguity on thermal degradation and the need for further results in this area.

4.1 | Specific factors

Graphene-TiO₂ (g-TiO₂) composites offer a narrow thermal window for calcination, which is necessary to remove organic residues and improve the crystallinity of TiO₂.^{116,117} However, calcination can lead to uncontrolled growth of TiO₂ nanoparticles, yielding larger crystallites and reducing the overall surface area. While a larger surface area is desirable for providing more reaction sites, it can also lead to imbalanced surface roughness and hinder charge transfer due to UV scattering.

Moreover, g-TiO₂ composites often tend to aggregate in suspension, which can hinder the injection of photoelectrons from TiO₂ into graphene. This aggregation leads to a rapid loss of active sites and subsequently lowers the photocatalytic activity of the composite material. Additionally, the agglomeration of graphene oxide (GO)/TiO₂ reduces the overall surface area, causing short-circuits, leakage current, and poor charge separation efficiency.^{118–123} The restacking of graphene sheets further reduces surface area and diminishes its useful electrical properties.

Furthermore, prolonged thermal stress during calcination may degrade the favorable interactions between

graphene and perovskite, potentially leading to a decrease in charge carrier mobility and efficiency of the ETL. This “burn-in” effect could compromise the performance of the PSCs by disrupting the electron transport pathways and reducing the effectiveness of charge extraction.

4.2 | Possible mechanisms of ETL enhancement by g-TiO₂

4.2.1 | Carrier generation and transport

The fundamental absorption principle requires that for photo-activity to occur, the incident photon energy be at least equal to the bandgap. The incorporation of graphene narrows the bandgap of TiO₂ into the visible range, making it easier to optimize the photovoltaic and photocatalytic efficiency in these wavelengths. The electron ground state is ideally in the graphene energy level, which falls within the TiO₂ bandgap. When this electron receives a photon, it enters the TiO₂ conduction band (CB), leaving behind a hole.^{123–125} In the p-i-n theory, the ideal separation of photo-generated e-h pairs for a high PCE occurs in opposite directions due to the depletion layer electric field. The graphene-TiO₂ composite are compatible because their energy levels are well-aligned energy, making efficient charge transfer and hole-blocking easier. This increases the device's open-circuit voltage, improves electron transport from perovskite to the ETL, and reduces charge recombination in defect centers. This is the accepted basic concept of high efficiency solar cells. Thus, band alignment, the nature of the graphene/perovskite interface and defects are crucial to overall device stability. The presence of the phenomenon of ferroelectricity at the interface also enhance PCE by expediting e-h separation and inhibiting their recombination at the photoactive interface.^{126,127}

4.2.2 | Photo-catalysis

Photo-catalysis is a fundamental absorption process that involves a UV photon ($\lambda < 390$ nm), as described above. The photo-excited electrons transfer to the surface of TiO_2 , react with oxygen dissolved in aqueous solution, producing a superoxide anion (O^{2-}). Meanwhile, the generated holes react with hydroxyl groups to form hydroxyl free radicals ($\text{OH}\cdot$). These radical products are strong oxidizing agents (electron donors) that decompose pollutant molecules into CO_2 and H_2O in processes that are effectively e-h recombination. Therefore, incorporating graphene promotes the separation of the e-h pairs in TiO_2 and thus improves photo-catalysis.¹²⁸

4.2.3 | Graphene-mitigated hydrophilicity

Hydrophilicity is an affinity for moisture that is dependent on incident photons and can lead to what is termed photo-induced super-hydrophilicity.¹²⁹ In this process, H_2O droplets can spread out in layers beneath thin films of TiO_2 in the presence of UV irradiation. This increases the number of hydroxyl groups attached to TiO_2 surfaces, raising the interesting potential to improve moisture rejection by indirectly employing some of the incident photon flux in an actual operating setting. Graphene is hydrophilic due to its highly oxygenated surface that facilitates interaction with aqueous dispersions of TiO_2 . This allows the formation of strong, chemically bonded g- TiO_2 nanocomposites. The directed localization of H_2O in layers outside of the photoactive interfaces controls to some extent the degrading effects of moisture.^{130,131}

5 | CONCLUSIONS

In this review, we have explored the potential of utilizing TiO_2 nanocomposite materials, incorporating pristine or selectively doped members of the graphene family, as electron transport layers (ETLs) in PSC applications. Beginning with a historical overview of TiO_2 -based solar cells, we progressed to discuss the contemporary state of doped TiO_2 PSCs, highlighting empirical limitations documented in recent literature. Emphasizing current critical issues facing PSCs, we then examine the potential benefits of g- TiO_2 nanocomposites as ETLs, including improved stability, durability, PCE, and reduced hydrophilicity, supported by empirical evidence from recent literature. Evaluating the latest contributions in the field, we aim to consolidate recent developments for enhanced repeatability. The thesis of this work underscores the clear potential for enhancing PSC devices through TiO_2

modification using various graphene family members. Specific improvements in PCE and long-term stability are important areas for future research, with emphasis on understanding photo-catalysis, photocurrent mechanisms, and hydrophilicity effects. This overview achieves a number of broad objectives. First, it highlights important gaps in the knowledge in the application of g- TiO_2 nanocomposites as effective ETLs. Second, it points out the significant directions for future investigations for the benefit of researchers and graduate students in this field in the hope of being a valuable resource of contemporary methods and materials.

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