

Recent Progress in Fe₂O₃–Graphene/TiO₂ Nanocomposite Photoanodes for Dye-Sensitized Solar Cells



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ABSTRACT

Dye-sensitized solar cells (DSSCs) remain a promising third-generation photovoltaic technology because of their low production cost, mechanical flexibility and good low-light performance. However, the efficiency of conventional TiO₂ photoanodes is limited by the wide band gap (≈ 3.2 eV), low electron mobility and charge trapping. Ternary nanocomposites combining TiO₂ with graphene derivatives, which improve electron transport, and Fe₂O₃ (2.0–2.2 eV), which extends visible-light absorption and aids charge separation, have therefore been proposed. This narrative review summarizes progress in the design and synthesis of Fe₂O₃-graphene/TiO₂ photoanodes for DSSCs, based mainly on literature published between 2020 and 2026. Hydrothermal, solvothermal, sol-gel, microwave-assisted, electrospinning and sonication routes are compared for scalability, structural control and component distribution, and characterization methods are related to structure-property-performance relationships. Key mechanisms, optimal loading and interfacial interactions are discussed. Direct photovoltaic evidence from fully integrated ternary photoanodes is very limited, and most quantitative data come from binary Fe₂O₃/TiO₂ or graphene/TiO₂ systems. The ternary architecture should therefore be regarded as a scientifically motivated hypothesis, based on complementary binary evidence that must be tested systematically under standard DSSC fabrication and testing conditions. Composition optimization, interface control, scalable synthesis and durability assessment are the main research priorities.

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INTRODUCTION

Global energy demand keeps on climbing as the population expands, urbanization continues, and industries grow, with fossil fuels still providing the majority of energy demand and being the primary source of carbon dioxide and other greenhouse gases (Osman et al., 2023).

Several renewable resources have been explored, but each has specific limitations: hydropower and geothermal are geographically constrained; wind energy is intermittent and site-specific; biomass competes with food production for arable land; and tidal/wave systems are expensive and restricted to certain coastal regions (Osman et al., 2023; Pourasl et al., 2023). Solar energy is

the least constrained, being clean, requiring no fuel supply chain, and available over most of the inhabited planet, with the scale of the resource being the determining factor (Al-Ali et al., 2025; Lewis & Nocera, 2006).

Solar energy can be harvested thermally or by photovoltaic (PV) conversion, which uses a semiconductor junction to create electrical power directly from photons, offering no working fluid, no thermodynamic cycle, no moving parts, silent operation, minimal maintenance, and scalability from milliwatt to gigawatt applications (Marzouk, 2025).

Despite this, PV conversion remains limited by technology, with challenges including manufacturing

cost and energy, the fraction of the solar spectrum convertible by a single absorber, recombination of photogenerated charge carriers, resistive and interfacial losses, degradation at high operating temperatures, sensitivity to shading and soiling, rigidity and weight of traditional glass-encapsulated modules, dependence on rare or toxic elements, and difficulty in material recovery at end of life.

First-generation PV based on crystalline silicon wafers provides high efficiency and long-term stability but requires high processing temperatures, thick absorber layers, and rigid, heavy modules (Azeez, 2024; Priya & Stonier, 2025). Second-generation thin-film PV (a-Si, CdTe, CIGS) reduces material usage and enables flexible formats but faces efficiency, toxicity, and supply

constraints (Priya & Stonier, 2025). Third-generation photovoltaics, including dye-sensitized solar cells (DSSCs), perovskite solar cells, quantum-dot solar cells, and organic photovoltaics (OPVs), use solution-processable, low-dimensional or molecular light harvesting systems that can be fabricated at low cost, offer mechanical flexibility, and have high optical absorption coefficients, making them attractive where rigid silicon modules are impractical (Azeez, 2024; Tayari et al., 2025). The drive toward nanometer-sized, low-dimensional structures is reflected in work on colloidal quantum dots, epitaxial nanostructures, and two-dimensional structures for optoelectronic applications including solar energy conversion (Salau et al., 2026).

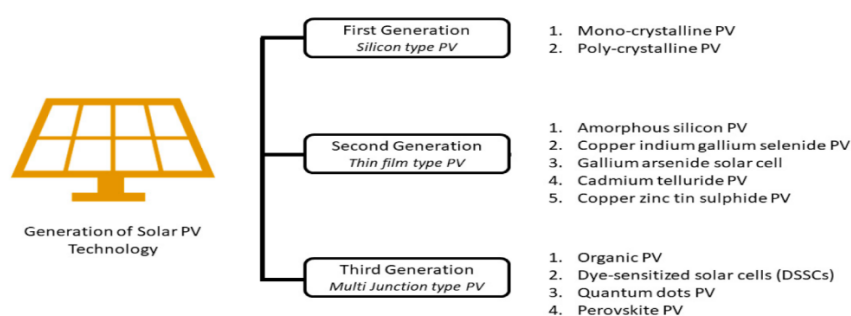


Figure 1: The global Development of Photovoltaic Technologies and the Role of DSSC within the First, Second, and Third Generation Photovoltaic Technologies (Ratnesh et al., 2025; Samsudin, 2023)

Figure 1 illustrates the position of these technologies in the overall path of PV development, showing the development of wafer-based crystalline silicon PV, thin-film PV absorbers, the emerging third-generation family of PV absorbers, and the role of DSSCs within this path. The figure is clear and 3 generations are differentiated not only by efficiency but also by the trade-offs they accept. First-generation devices provide high efficiency and long-term stability at high use of materials, high processing energy, and high mechanical rigidity. Second-generation devices stop using less material and allow flexible formats, but sacrifice optimized efficiency or, in some instances, introduce toxicity or element scarcity issues. The third generation of devices, like the DSSCs, have taken a hit in peak efficiency, but in return they are manufactured using low-temperature solution-based processes, are mechanically flexible, and exhibit greater tolerance for diffused or low-intensity illumination than the first generation of devices. So, the reason for the present review is that DSSC cannot yet out-compete the crystalline silicon competitor in large-scale generation, but it can be seen to cover a niche of application (indoor, portable, wearable, building-integrated power generation) that silicon does not seem to fill well, and this is where its photoanodes have to improve.

In regard to 3rd generation technologies, DSSCs have been drawing attention since O'regan and Grätzel invented the device architecture in 1991 (O'regan & Grätzel, 1991; Ratnesh et al., 2025; Samsudin, 2023). The light absorption is carried out by a molecular dye, and the transport of charges is carried out by a wide-bandgap mesoporous semiconductor to which the dye is adsorbed; as a result of this separation, a DSSC gets energy from captured photons. This separation is the key to the low costs of the technology, as it means there is no need to employ a high-purity defect-free semiconductor absorber. Few photovoltaic technologies are capable of such low-temperature, solution-based manufacturing, can be applied to a variety of substrates and, due to their superior performance under diffuse low-intensity indoor lighting relative to full sun, can yield an entire new range of application areas that other outdoor-based panels are unable to satisfy.

Much of the current research effort is focused on improving the efficiency of the cells, reproducibility of the fabrication, their durability, and cost. In particular, flexible DSSCs have been the subject of investigation, as a light and bendable device can be optimized for portable, wearable, and building-integrated applications; alternatives to rigid glass substrates, which enable low-temperature processing and large-area manufacturing,

are all available and allow the system to be light and conformable (Abdulsalami et al., 2026; Bella et al., 2015).

In the DSSC, the influence of the photoanode on performance is disproportionate, as it has two tasks to undertake. It provides the volume in which dye can be adsorbed onto the scaffold, and it gives the path by which the electrons flow to the transparent conducting substrate after they have been photoinjected into the dye scaffold. The ideal characteristics of the photoanode for dye absorption should therefore include photochemical and chemical stability, a high electron mobility, the correct band-edge positions relative to the dye and redox couple, and a high surface area. (Lana et al., 2024; Rahman et al., 2023).

Titanium dioxide (TiO₂) is the most thoroughly researched material with these specifications, with anatase TiO₂ being the current standard. It has favorable band-edge positions, chemical stability, corrosion resistance, is naturally abundant, is cost-effective, is not inherently toxic, and can easily be fabricated into mesoporous nanostructures providing a high internal surface for the adsorption of dyes and the harvesting of light (Hagfeldt & Vlachopoulos, 2018; Yuan et al., 2024). It also has its limitations. It has a band gap of the order of 3.2 eV, which constrains its ability to absorb practically only the UV band, whilst the dye would absorb essentially all visible light, a relatively small electron mobility and the ability to trap electrons in grain boundaries and surface defects before reaching the collecting electrode, where they can recombine with an oxidized dye molecule or with the redox electrolyte. These losses cause a decrease in the short-circuit current density, the open-circuit voltage, and the overall power conversion efficiency, and are what makes that unmodified TiO₂ photoanodes no longer considered to be the ultimate goal in the design of photoanodes (Hagfeldt & Vlachopoulos, 2018; Lana et al., 2024; Yuan et al., 2024; Olaniyi et al., 2023).

To overcome the limitation of transport, graphene has been a highly successful additive. It has an exceptionally high carrier mobility up to $\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, excellent electrical conductivity, high optical transparency $\sim 97.7\%$ for monolayer), a large theoretical surface area $\sim 2630 \text{ m}^2 \text{ g}^{-1}$ and quite high mechanical strength, which has made it attractive in all electronic, optoelectronic, and energy-conversion devices [18-20]. In the photoanode, these properties enable graphene to interweave the conductive network into the TiO₂ matrix to boost the extraction speed of electrons, eliminate the charge transfer resistance, inhibit charge recombination, and enhance the mechanical strength of the composite film (Gusain et al., 2024; Ratnesh et al., 2025; Yuan et al., 2024).

The top-down routes are more appealing than the bottom-up methods due to their simplicity, low costs, scalability, and reproducibility; particularly the oxidation-reduction

route, which produces graphene oxide (GO) and reduced graphene oxide (rGO). Of the three, the oxidation-reduction route is the most popular as it makes functionalization simple and enables close coupling between graphene derivatives and a range of semiconductor nanomaterials including TiO₂ (Bhuyan et al., 2016; Gusain et al., 2024).

However, by enhancing electron transport alone, this optical limitation with TiO₂ cannot be solved. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has thus been studied as an alternative modifier. It has a medium-sized band gap of about 2.0 – 2.2 eV that captures a significant fraction of the visible spectrum that TiO₂ cannot capture and has low cost, is non-toxic, naturally occurring, stable, and corrosion-resistant. Note that the positions of the conduction and valence bands allow the creation of heterojunctions with TiO₂ in which photogenerated carriers are spatially separated and the transfer of electrons are transferred. In addition, the Fe₂O₃ nanoparticles are able to change film morphology, thus enhancing dye adsorption and internal light-scattering (Rahman et al., 2023; Rani et al., 2019). The electron mobility in pristine Fe₂O₃ films is extremely low (Lana et al., 2024; Munien et al., 2026; Rani et al., 2019) due to a very short hole diffusion length, and the rate of recombination of carriers is very high, which limits the utilization as a stand-alone photoanode.

The shared conclusions of these observations center on the ternary Fe₂O₃–graphene/TiO₂ photoanode, where the mesopores in the TiO₂ framework are excellent dye anchor sites and electron injection sites, while the graphene provides very rapid charge transport, and the Fe₂O₃ increases the amount of visible light absorbed and heterojunction-assisted charge separation. The three components cover complementary loss mechanisms, and thus, the assignment to the three mechanisms should be better than to the two binary systems. In practice, the evidence for this is incomplete, and defining what is in fact known is the aim of the present review.

To date, DSSC photoanode research has followed three largely independent paths: (1) crystal structure and morphology engineering of TiO₂; (2) incorporation of graphene, graphene oxide (GO), or reduced graphene oxide (rGO) into TiO₂ to enhance electron transport and reduce recombination; and (3) employment of iron oxide, principally hematite ($\alpha\text{-Fe}_2\text{O}_3$), to shift the optical response into the visible spectrum and create heterojunctions. Each path has produced measurable gains. However, the majority of studies concern binary systems: Fe₂O₃/TiO₂ (Da Cunha et al., 2026) or graphene/rGO- TiO₂ (Anish Madhavan et al., 2012; Dang et al., 2021; Makal & Das, 2021; Peiris et al., 2021; Singh et al., 2022; Tang et al., 2018; Yang et al., 2010). Fully integrated ternary Fe₂O₃–graphene/TiO₂ photoanodes for DSSCs remain scarce. The only closely related ternary study (Botsa, 2025) applied the composite to photocatalytic degradation of nitrobenzene and dye

pollutants, not to DSSCs, and reported no photovoltaic parameters. Therefore, the ternary architecture should be regarded as a scientifically motivated hypothesis supported by complementary binary evidence, requiring systematic experimental validation in DSSC configuration.

What has not yet been done is to consider these three materials as one cohesive system, co-designed for one another. The survey and comparison between existing review literature is due to the majority of the works reporting broad surveys of the total DSSC technology or focused treatments on one binary pair: TiO₂/rGO, Fe-modified TiO₂, or graphene/TiO₂ for photocatalysis rather than photovoltaics. To the best of our knowledge, no previous report has focused on the Fe₂O₃–graphene/TiO₂ ternary photoanode and raised the intriguing questions of how, and under what conditions, the three components complement each other.

This review fills this gap and is new in the following five aspects. First, it provides a concise definition of the roles that each of the three components plays, namely TiO₂ as the mesoporous dye-anchoring scaffold and electron acceptor, graphene as the low-resistance transport network, and Fe₂O₃ as the heterojunction modifier for visible-light, and correlates their functions with measured photovoltaic parameters. Secondly, the data on the Fe₂O₃-modified and graphene-modified TiO₂ photoanodes from reported studies are summarized in a single comparative table (Table 1), which clearly shows that this non-monotonic dependence does not change across independent studies. Third, it is a structured comparison of the previous reviews and research pieces in the ternary photoanode-approaching literature, wherein it explains what was covered, what was not, and how it differs from the explicit positioning that the existing literature on ternary photoanodes does not provide. Fourth, it structures available preparation routes in a synthesis-strategy taxonomy, connecting them with structural attributes that they control and scaling limits of their use. Nevertheless, it includes, in its fifth section, practical and verifiable directions for future research, such as standardization of the reporting, which would allow the comparison of studies.

This review does not give the reason why ternary is already proven to be a better structure. It is that studies of the composition–interface–transport–performance relationship of Fe₂O₃–graphene/TiO₂ photoanodes are insufficiently characterized; the available evidence identifies critical parameters that require systematic investigation, and the ternary system should be investigated systematically rather than incidentally.

In this review, the latest developments in photoanodes for DSSCs consisting of Fe₂O₃–graphene–TiO₂ are summarized, reported, and highlighted from the literature published from 2020 to 2026. The working principle of the DSSC and the role of the photoanode in the DSSC are

explained and summarized in Section 2. In Section 3, the three components of the photoanode are considered separately: the host semiconductor TiO₂, the conductive additive graphene and its derivatives, and the modifier Fe₂O₃, which is active under visible light. Section 4 discusses the ternary composite material itself, including the synergistic principles, the main synthesis methods, and the methods of characterization for the correlation between structure and performance. Section 5 is the assembly of reported photovoltaic results, which compares them. Section 6 compares this work with the available review literature, while Section 7 identifies the research gaps, challenges, and prospects in the field based on the analysis.

Literature Search and Selection Methodology

This work is a narrative review with systematic elements. It is not intended as a fully systematic review with meta-analysis. The literature search was conducted to identify studies relevant to Fe₂O₃-graphene/TiO₂ ternary photoanodes for DSSCs, with emphasis on publications from 2020 to 2026.

Databases searched include Scopus, Web of Science, Google Scholar, and PubMed and the following combinations of keywords were used: ("dye-sensitized solar cell" OR "DSSC" OR "dye sensitized solar cell") AND ("TiO₂" OR "titanium dioxide") AND ("graphene" OR "reduced graphene oxide" OR "rGO" OR "graphene oxide" OR "GO") AND ("Fe₂O₃" OR "iron oxide" OR "hematite" OR "α-Fe₂O₃"); ("ternary photoanode" OR "ternary nanocomposite") AND ("DSSC" OR "dye-sensitized solar cell"); ("Fe₂O₃/TiO₂" OR "iron oxide modified TiO₂") AND ("DSSC" OR "photoanode"); ("graphene/TiO₂" OR "rGO/TiO₂") AND ("DSSC" OR "photoanode"). The primary data search literature was conducted in January 2026, with updates through March 2026.

Inclusion criteria (1) Peer-reviewed journal articles, review articles, and conference proceedings; (2) studies reporting DSSC photoanodes based on TiO₂ modified with Fe₂O₃ and graphene derivatives; (3) studies reporting at least one photovoltaic parameter (Jsc, Voc, FF, or PCE); (4) studies published in English; (5) studies published between 2020 and 2026 for photovoltaic performance data, with foundational earlier works included for theoretical context.

Exclusion criteria (1) Studies focused exclusively on photocatalysis without DSSC photovoltaic data; (2) studies not reporting any photovoltaic parameters; (3) studies on DSSC components other than the photoanode (counter electrode, electrolyte, dye) unless directly relevant to photoanode design; (4) non-peer-reviewed sources; (5) non-English publications.

Titles and abstracts were screened for relevance. Full texts of potentially relevant articles were then assessed against inclusion and exclusion criteria. Reference lists

of retrieved articles were also checked for additional relevant studies (snowballing).

The search identified approximately 320 records. After removal of duplicates and screening of titles and abstracts, 87 full-text articles were assessed. Of these, 24 studies met the inclusion criteria and were retained for detailed analysis. Importantly, only one study (Botsa, 2025) was identified that investigated a ternary Fe₂O₃-graphene/TiO₂ composite, and that study was photocatalytic rather than photovoltaic. All other retained studies investigated binary systems (Fe₂O₃/TiO₂ or graphene/TiO₂).

Photovoltaic parameters (J_{sc} , V_{oc} , FF, PCE), synthesis method, optimum loading, dye type, electrolyte type, and key observations were extracted from retained studies. Data were tabulated (Table 1) for comparison. Because of differences in dyes, electrolytes, photoanode thickness, TiO₂ morphology, fabrication methods, measurement area, and measurement conditions, direct quantitative comparison across studies is limited. The comparison is therefore qualitative and is intended to identify trends and knowledge gaps rather than to provide a definitive ranking of performance. Studies were also classified by type of evidence (direct ternary, indirect binary, or ternary non-DSSC) in Table 3.

The review methodology is limited by the scarcity of direct ternary DSSC studies, the heterogeneity of reported fabrication and testing conditions, and the inconsistency of reporting across studies. Some studies did not report all photovoltaic parameters (e.g., FF or V_{oc}), further limiting comparison. The conclusions of this review should be interpreted with these limitations in mind.

Basic Working Principle of Dye-Sensitized Solar Cells

The basic working principle of DSSCs is described in this section. The five key components of a DSSC are: a transparent conducting oxide (TCO) substrate, a semiconductor photoanode, a dye sensitizer, a redox electrolyte, and a counter electrode. The photoanode and counter electrode are usually deposited on TCO glass, commonly fluorine-doped tin oxide (FTO) or indium tin oxide (ITO), which act as the working and counter electrodes, respectively. The entire assembly is compressed, and the electrolyte is introduced between the two electrodes to conduct the charge from one electrode to the other (Korir et al., 2024; Rahman et al., 2023).

Every part has a specific function, and it is the combination of these functions that will dictate the cell's

overall function. The photoanode can serve as a high surface area scaffold for dye adsorption and acts as the electron transport pathway. The dye sensitizer absorbs incoming solar energy, the electrolyte rejuvenates the oxidized dye and transports the charge between the electrodes, and the counter electrode catalyzes the reduction of the electrolyte and completes the electrical circuit.

Dye molecules attached to the photoanode surface absorb photons. This excitation promotes the dye electrons to an excited state, and they are quickly injected into the conduction band of the semiconductor, typically TiO₂, which has an appropriate electronic structure and chemical stability. Upon injection, the electrons flow through the network of interconnected TiO₂ particles and arrive at the transparent conducting substrate, pass through the external circuit where they discharge to perform useful electrical functions, and finally arrive at the counter electrode.

In the meantime, the oxidized form of the dye is reduced back to the original form by accepting electrons from the redox electrolyte, iodide/triiodide (I^-/I_3^-). The resulting triiodide is transferred by the electrolyte to the counter electrode, where it is reduced to iodide by electrons from the external circuit. This process of photon absorption, electron injection, charge transport, and dye-electrolyte regeneration continues to generate electricity from sunlight as long as the cell is illuminated (Lana et al., 2024; Rahman et al., 2023).

The efficiency of the DSSC in converting sunlight all the way down to the conversion of the electron from the semiconductor into the electrode is rooted in the efficiency of these charge transfer steps. High performance requires efficient electron injection, rapid electron transport in the photoanode, effective dye regeneration, and minimal recombination; for most photoanodes, the rate of electron transport through the semiconductor is the rate-limiting process. The electron mobility of conventional TiO₂ photoanodes is low, and there is large recombination due to trapping at grain boundaries and surface defects. That is why many efforts have been made to modify the photoanodes of TiO₂ with conductive nanomaterials such as graphene and its derivatives to enhance electron transport, reduce electron-hole recombination, and increase the power conversion efficiency (Korir et al., 2024; Lana et al., 2024; Rahman et al., 2023).

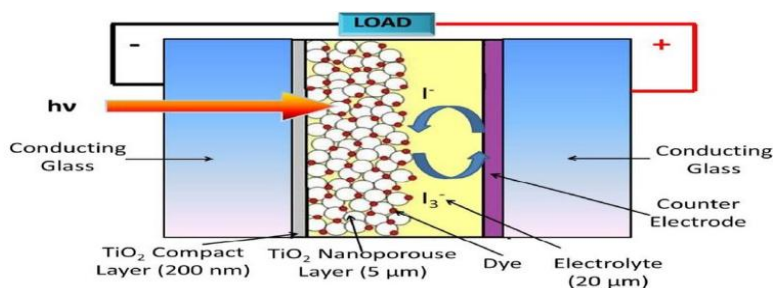


Figure 2: Structure and Working Principle of a Dye-sensitized Solar Cell (DSSC)(Baig, 2021)

The above structure and functioning are summarized in Figure 2. The cell structure sketched above, with a transparent conducting substrate, a composite (translucent) semiconductor photoanode coated with dye molecules, a redox electrolyte, and a catalytic counter electrode, makes explicit the fact that the DSSC is a regenerative cell, where all components remain unchanged when the device is excited, injected, transported, and regenerated to its initial state (Baig, 2021). There are two points about the figure that are immediately pertinent to the design of the photoanode. First, the path of the electron from the point of injection to the external circuit is always confined to the mesoporous semiconductor network: the properties of the mesoporous network, and not the optical properties of the dye, typically determine the maximum current collected. Second, the photoanode has to be continuous throughout the thickness, and therefore any point on the electron pathway can be a point at which back transfer can occur to the oxidized dye or the triiodide species. Increasing the speed of the passage of electrons through the network and increasing the probability of their survival on the way are two aspects that would improve the photoanode. This is the "dual requirement" that the next two sections of the presentation discuss: 3.0 graphene and Fe₂O₃ modifications, respectively.

In a DSSC, the conversion of sunlight to electricity primarily occurs at the surface of the semiconductor photoanode that also performs two functions: it supports the dye molecules and acts as a conduit for the transport of electrons generated by the dye to the transparent conducting substrate. This dual functionality means that the material of the photoanode has a disproportionately strong influence on the device performance. To effectively collect charges, an ideal photoanode should have a high specific surface area for dye loading, a proper band alignment, high chemical stability, high electron mobility, and low recombination (Lana et al., 2024; Rahman et al., 2023).

So far, TiO₂, particularly the anatase form, is the most frequently used material for a photoanode due to its chemical stability, low toxicity, adequate availability, resistance to corrosion, low cost, and compatibility with a large number of dye sensitizers. The mesoporous

nanostructure allows for a large surface for dye loading and efficient light harvesting, and that is why it is the benchmark semiconductor for DSSC work (Korir et al., 2024; Lana et al., 2024).

Nevertheless, pure TiO₂ is not without its drawbacks: its electron mobility is fairly low, and the surface defects and grain boundaries trap electrons, leading to high charge losses. The electrons that pass through the network of TiO₂ nanoparticles can recombine with the oxidized form of the dye molecules or with the redox species present in the electrolyte, without reaching the collecting electrode. The suppression of recombination is one of the most important remaining problems in improving the performance of the TiO₂ photoanode, as it can reduce the short-circuit current density, open-circuit voltage, and therefore the overall power conversion efficiency of the cell.

Various approaches have been used to overcome these constraints, such as doping, morphology engineering, heterojunction creation, surface passivation, and blending with conductive carbon nanomaterials. Of these, graphene and its derivatives are the most promising, due to their excellent conductivity, very high carrier mobility, high surface area, and strong interfacial charge transfer behavior. TiO₂/graphene nanocomposite photoanodes are one of the most intensely studied configurations in next-generation DSSCs, as they have been consistently demonstrated to enhance electron transport, reduce recombination losses, promote charge collection, and increase overall PV performance (Gusain et al., 2024; Korir et al., 2024; Lana et al., 2024).

Photoanode Materials for DSSCs

Three material functions are necessary to obtain good performance of a DSSC photoanode that are never simultaneously accomplished by a single semiconductor material: high surface area, a chemically stable scaffold for anchoring the dyes and injecting the electrons; rapid, low-cost transport of injected electrons to the collecting substrate; collection of the visible portion of the solar spectrum that is not captured by the dye. This section looks at the three materials which are used in combination to fulfill these requirements one by one, in the order they come into the design. The level of

performance and the shortcomings that justify its modification are determined by the properties of the host semiconductor, TiO₂, which is considered in Section 3.1. In Section 3.2, graphene and its derivatives are discussed as a primary solution to the TiO₂ transport and recombination problems. Fe₂O₃ is introduced in Section 3.3 for its main optical limitation. When one thinks of the components in the following order, it is easier to appreciate why the ternary composite (Section 4) takes this form.

Titanium Dioxide (TiO₂) as a Photoanode Material

TiO₂ still remains the standard material to be used for the photoanode in DSSCs because of its good physical and chemical properties and the ability to use dye sensitizers. Zinc oxide (ZnO) has higher intrinsic electron mobility, but its use in DSSCs is hampered by poor chemical stability in acidic dye solutions and lower dye adsorption capacity (which adversely affect the performance). However, TiO₂ remains the most commonly used research and commercial material due to its stability, availability, low cost, nontoxicity, corrosion resistance, and optimum energy band gap matching to the common sensitizing dyes (Hagfeldt & Vlachopoulos, 2018; Lana et al., 2024; Yuan et al., 2024). Of the three naturally occurring crystal structures of TiO₂ rutile, anatase, and brookite, anatase is the most commonly used for DSSC photoanodes, primarily due to its conduction band position, moderate surface area, and electron injection properties? The nanoparticles of anatase TiO₂ have a large internal surface area for dye loading and efficient pathways for charge collection, and are ideal for charge collection and light harvesting (Lana et al., 2024; Yuan et al., 2024).

Even pristine TiO₂ can have its limitations. Because of its band gap of about 3.2 eV, TiO₂ absorbs very little visible light, meaning that the dye must do the majority of the work to absorb the visible light. It also has a relatively low electron mobility and a large number of grain boundaries and surface defects where electrons are trapped and recombine before reaching the collecting electrode, reducing photocurrent, open-circuit voltage, and total power conversion efficiency (Hagfeldt & Vlachopoulos, 2018; Lana et al., 2024; Yuan et al., 2024). These problems have been approached from various perspectives, such as controlling morphology, tuning the crystal phase, doping, heterojunctions, surface passivation, and the addition of conductive nanomaterials. A range of one-dimensional nanorods, nanotubes, and nanowires have been investigated, as have been a variety of hierarchical porous and mesoporous architectures for better electron transport, more dye loading, more effective light scattering, and a reduction in recombination. Carbon nanomaterials such as graphene and its family members have recently been the focus of interest for their role in the fabrication of

efficient electron transport networks in TiO₂ photoanodes (Lana et al., 2024; Yuan et al., 2024).

Graphene and its Derivatives in TiO₂ Photoanodes

Graphene and its derivatives have become promising multifunctional materials for boosting DSSC performance. Their exceptional conductivity, very high carrier mobility, strong optical transparency, large theoretical surface area ($\approx 2630 \text{ m}^2 \text{ g}^{-1}$), and impressive mechanical strength have led researchers to try graphene-based materials in nearly every part of the DSSC: the counter electrode, the electrolyte, the transparent conducting electrode, and the photoanode itself (Gusain et al., 2024; Lana et al., 2024; Rahman et al., 2023).

Early studies mostly looked at graphene as a low-cost, catalytically active alternative to platinum counter electrodes, and separately as an additive to improve the ionic conductivity and stability of electrolytes. These studies confirmed graphene's versatility across the device, but attention has gradually turned toward its use in the semiconductor photoanode, which is widely regarded as the component that most directly governs electron generation, transport, and collection (Korir et al., 2024; Lana et al., 2024; Rahman et al., 2023).

The dual role of the photoanode, as a surface area for adsorption of the dye and the primary electron conduction path, is the focus of research to increase the conductivity of the photoanode and reduce the recombination effect. Graphene is well suited to this purpose and also meets the following requirements: excellent conductivity for the rapid transport of electrons, high optical transparency so that a large portion of light can penetrate to the dye, and high mechanical strength and flexibility, which is suitable for both rigid and flexible devices. It is also electronically tunable and therefore can interact effectively with TiO₂ nanoparticles at the interface, which hinders the recombination loss of charges (Korir et al., 2024; Lana et al., 2024; Rahman et al., 2023).

The first use of graphene as a photoanode component was in a solid-state DSSC, as a transparent conducting electrode (Das et al., 2014). The graphene electrode achieved electrical conductivity of $\sim 550 \text{ S/cm}$ and optical transparency of $>70\%$. The resulting device obtained only a power conversion efficiency (PCE) of 0.26%, far behind the 0.84% obtained with an FTO-based device, but the study laid the foundations for future studies on graphene-modified photoanodes. Since then, research has progressed much further than working with graphene alone as an electrode, and is now focused on nanocomposite photoanodes of TiO₂.

Later studies used a transparent conducting substrate that contained graphene, graphene oxide (GO), or reduced graphene oxide (rGO) within the TiO₂ photoanode to accelerate the transport of charge carriers and enhance

the collection of charge carriers while reducing charge carrier recombination. These composite photoanodes have always shown better performance than pure TiO₂, but the improvement varies significantly with the amount of graphene loading, composite construction, synthesis technique, and the engineering of the interfaces (Korir et al., 2024; Lana et al., 2024; Rahman et al., 2023).

More recent work has shown that graphene does more than simply conduct; it also acts as an interfacial charge transfer medium. When TiO₂ nanoparticles are in close contact with graphene sheets, conductive pathways are formed for the quicker transfer of electrons to the collecting electrode, and the trapping and recombination of the electrons are reduced. Moreover, graphene is able to disperse TiO₂ nanoparticles uniformly and enhance the mechanical properties of the composite film, contributing to its structural stability. These effects combined lead to increased photocurrent density, increased electron lifetime, and improved overall power conversion efficiency (Lana et al., 2024; Yuan et al., 2024).

Since then, the field has shifted from basic binary TiO₂/graphene composites to more advanced designs

including ternary systems of additional semiconductors or dopants, three-dimensional networks of graphene, and hierarchical porous composites. Such architectures not only achieve better electron transport, but also better dye loading, light harvesting, and interfacial charge separation, mitigating many of the drawbacks of single TiO₂ photoanodes (Lana et al., 2024).

Challenges remain, however. The challenges remaining are still open issues with respect to the uniform distribution of graphene, loading quantity, and avoiding sheet restacking, and the engineering of a stable TiO₂/graphene interface, which can impact the reproducibility and device performance under study. The range of PV efficiencies reported by different studies further indicates that the advantages of the composite will be strongly dependent on the synthesis and structure of the composite. In the future, the field will be directed towards more functional ternary nanocomposites that can simultaneously enhance light harvesting, charge separation, electron transport, and long-term stability properties, as well as towards smarter interface engineering and more scalable synthesis routes.

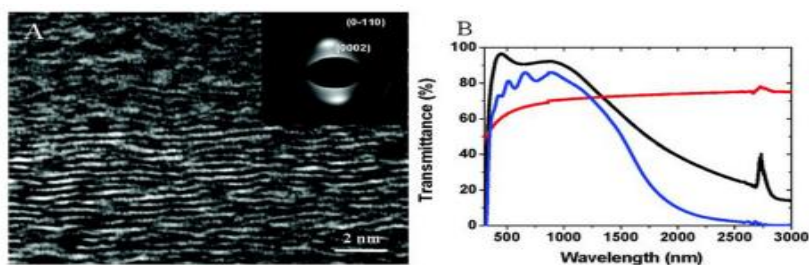


Figure 3: (A) HRTEM Image of Graphene Films and the SAED Pattern (Inset) Obtained from the Image. (B) Transmittance of a ca. 10 nm Thick Graphene Film, Compared to ITO Film (Black) and FTO Film (Blue) (Wang et al., 2008)

Figure 3 serves as the experimental foundation for the potential use of graphene as a photoanode material and not just a desired material in concept. As evident in the high-resolution transmission electron micrograph shown in Figure 3(A) and the selected area electron diffraction pattern displayed in the inset, the deposited films show the crystalline lattice of graphene, with the clear diffraction spots confirming that the structures are highly ordered and are sp² carbon and not amorphous carbon deposits, a condition essential for the high carrier mobility that is the basis for the transport function. The competition between optical transparencies, as in Figure 3 (B), is addressed in the present invention. A graphene film about 10 nm thick transmits across the visible range at a level similar to that of the two different reference films ITO and FTO measured with it. The implications for the design of the photo-anodes are that these two properties, conductivity and transparency, are generally conflicting, as thicker layers of most conductive materials generally result in less light reaching the dye. It

is evident from Figure 3 that in the case of graphene, there is virtually no trade-off, thus allowing it to be added to the optical path of a photoanode without any of the parasitic absorption losses that would be incurred by a comparable thickness of a conventional conductor.

Due to its extremely high carrier mobility, high conductivity, large surface area, and excellent mechanical strength, graphene has proven to be a good choice for a conductive scaffold. It is then incorporated into the TiO₂ and creates interconnected pathways that increase the rate of electron transport, reduce recombination, and enhance electron collection. It also disperses evenly TiO₂ nanoparticles and enhances the charge transfer at the semiconductor-transparent conducting substrate interface. The TiO₂/graphene nanocomposite photoanodes have superior properties compared to pristine TiO₂ and are one of the most intensively studied material systems for next-generation DSSCs (Gusain et al., 2024; Lana et al., 2024; Rahman et al., 2023).

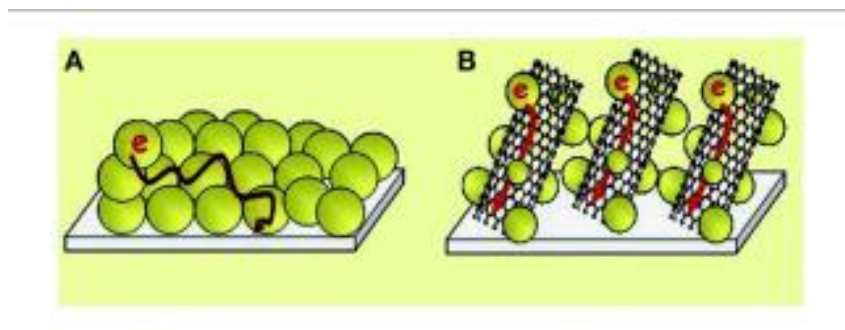


Figure 4: Electron Transport through Pure TiO₂ Nanoparticles (A) Versus across CNTs (B) (Kongkanand et al., 2007)

Carbon nanomaterials in general have been widely tested as conductive additives to make up for pristine TiO₂'s shortcomings. It was early proven that carbon nanotubes (CNTs) could provide an electron pathway with short diffusion distances, minimizing electron-hole recombination within the TiO₂ network. The advantage of CNT-assisted TiO₂ photoanodes lies in their capability to reduce recombination events, as shown in Figure 4 when electrons are being transported through the photoanode, compared to the pristine TiO₂ nanoparticle network (Kongkanand et al., 2007).

One reason for the stark changes in the behaviour of the photoanode as a result of the introduction of a conductive additive can be seen from the contrast in Figure 4. The injected electron has to travel a many-hop path in the pristine TiO₂ nanoparticle network of Figure 4(A), and at every grain boundary it can both block electron migration and offer a possible trap state; these hops are long, diffusive, and repeatedly stalled by migration to a new trap state, to be followed by extensions to recombination with the oxidised dye or the electrolyte. In Figure 4(B), the electrode material is a continuous conductive strip; the carbon nanotube scaffold provides a continuous conductive path for the electron to enter and easily flow straight to the collecting substrate and avoid most of the electrode boundaries. The actual improvement realized with a conductive additive is less due to the increase in the intrinsic mobility of TiO₂ than due to the decrease in the time the electron may spend in the conducting network, because loss of mobility through recombination in the conducting network is a function of the time that the electron is in that network.

Although these are encouraging, graphene has slowly replaced CNTs as a material choice, primarily due to its 2D geometry. Graphene sheets have much higher surface area than one-dimensional CNTs, which promotes the dispersion of TiO₂ nanoparticles, enhances the interfacial contact, and establishes continuous conductive pathways for electron transfer. These properties enhance electron extraction from the photoanode, recombination suppression, and charge collection in the photoanode (Gusain et al., 2024; Lana et al., 2024; Yuan et al., 2024). To boost the PCE, Yang et al. (Yang et al., 2010) have introduced reduced graphene oxide (rGO) on TiO₂ photoanodes, which resulted in an increase in the short-circuit current density (*I*_{sc}) from 3.35 to 11.26 mA cm⁻² and power conversion efficiency (PCE) from 0.58% to 5.01%, thereby demonstrating that the addition of graphene enables the acceleration of electron transport. With a lateral size of approximately 0.2–2 μm, the rGO sheets served as conducting networks throughout the TiO₂ matrix, which led to better electron transfer and less recombination losses.

Subsequent research has concentrated on optimizing the graphene content, on controlling the TiO₂/graphene interface, and on designing hierarchical nanostructures to further enhance the performance. Well-designed TiO₂/graphene nanocomposites have been found to enhance the dye loading, increase the electron lifetime, accelerate charge transport, and increase the power conversion efficiency significantly higher than that of pristine TiO₂, which makes graphene one of the most widely studied conductive nanomaterials for next-generation DSSC photoanodes (Lana et al., 2024; Rahman et al., 2023; Yuan et al., 2024).

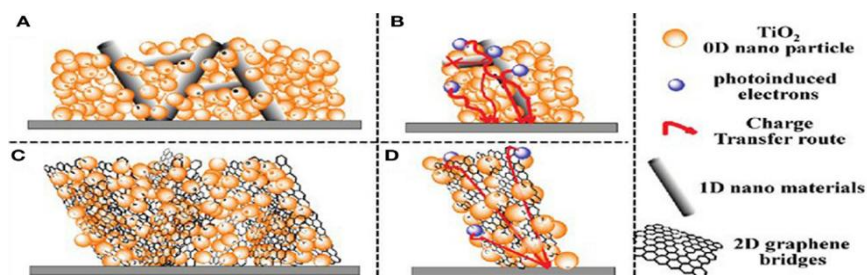


Figure 5: Comparison of Material Loading and Electron Transport across CNT (A, C) and through Graphene Sheets (B,D) (Yang et al., 2010)

To compare carbon nanotubes with graphene, and to show the material preference that ensued, see Figure 5. In one-dimensional CNTs (panels (A) and (C)), in which TiO₂ nanoparticles contact the nanotube in a line, each conductive element only contacts the particles neighbouring it, and a conductive network is established where individual tubes happen to percolate. Two-dimensional Panels (B) and (D) depict the equivalent scenario for graphene sheets; being contacted on a plane instead of along a line; a single sheet of graphene can support a large number of TiO₂ nanoparticles across a significantly broader surrounding matrix, and also achieves continuity by itself, despite 1D graphene tubes depending on percolation to accomplish the same. This dimensionality difference is the primary factor that led to the gradual replacement of CNTs with graphene as the most convenient conductive additive in DSSC photoanodes for the three observed advantages: increased loading of materials per unit of conductive additive, uniform distribution of the TiO₂ nanoparticles, and reduced fraction of additive for the formation of the continuous transport network. It also details the sensitivity to loading seen across Table 1: each of the above loadings is effective over a large area, so the loading is not particularly critical, and excess loading above the optimum point introduces new graphene–TiO₂ interfaces that serve as recombination sites instead of useful pathways to transport the charge current.

After the first demonstrations of graphene-enhanced TiO₂ photoanodes, much of the follow-up work aimed at improving how well graphene and the semiconductor materials bond and interact. One of the earliest approaches was simply dispersing commercial TiO₂ (P25) nanoparticles into polymer-supported graphene water/ethanol suspensions to make composite photoanodes with better conductivity and charge transport. These studies confirmed that graphene could establish conductive pathways inside the TiO₂ network, speeding electron transport and reducing recombination (Yang et al., 2010).

To strengthen the TiO₂ graphene interface further, Yang et al. (Yang et al., 2010) built large-area rGO/TiO₂ composite photoanodes on ITO substrates using molecular assembly and electrophoretic deposition.

Functionalization of the graphene oxide (GO), obtained by the modified Hummers' method, was carried out with titanium butoxide, and then it was reduced by hydrolysis to attach it more strongly to the TiO₂ nanoparticles. The resulting photoanodes were sensitized with the standard N719 dye and exhibited a higher conductivity than the pristine TiO₂ and achieved a short-circuit current density (J_{sc}) of 6.67 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.56 V, a fill factor (FF) of 0.45, and a PCE of 1.68%.

Subsequent research used various nanostructures of TiO₂ to further boost performance. To enhance surface area and electron transport, Madhavan et al. (Anish Madhavan et al., 2012) incorporated graphene into electrospun TiO₂ nanofibres. The graphene-modified nanofibre photoanode efficiency of 16.2 mA cm⁻², V_{oc} of 0.71 V, FF of 0.66, and PCE of 7.6% was an improvement over the pristine TiO₂ nanofibre photoanode, which produced an efficiency of 13.9 mA cm⁻², V_{oc} of 0.71 V, FF of 0.63, and PCE of 6.3%. These figures highlight how beneficial graphene is in enhancing charge transport and PV efficiency.

In addition to the ordinary TiO₂ nanocrystals, graphene has been combined with other semiconductor structures that have been designed to enhance electron mobility, dye adsorption, and reduce the recombination rate due to better electron transfer at the interfaces [28], such as TiO₂ nanosheets, TiO₂ interlayers, NiO/graphene composites, and ZnO nanorod/graphene hybrids. Building on this, Bell et al. and Wang et al. looked at the impact of the intrinsic loading of graphene on PV performance.

Both studies found that small amounts of graphene markedly improved electron transport in TiO₂ photoanodes, with Wang et al. reporting that around 0.7 wt% graphene gave the best power conversion efficiency. At lower loadings, graphene builds useful conductive pathways that speed up electron extraction; push the loading too high, however, and the growing number of graphene TiO₂ interfaces starts creating extra recombination centres that hurt performance instead (Lana et al., 2024).

Later work on optimizing graphene-modified TiO₂ photoanodes also looked at controlling the semiconductor's morphology specifically, how TiO₂ particle size and photoanode thickness affect charge

transport. Using conductive atomic force microscopy (c-AFM) and nano current–voltage measurements, researchers found that smaller TiO₂ particles produce a more continuous conductive network within the graphene TiO₂ composite, improving electron mobility and enabling more efficient charge transport.

Taken together, this body of early work established the scientific case for graphene-modified TiO₂ photoanodes and showed that adding graphene can meaningfully improve electron transport, suppress recombination, and raise the photovoltaic performance of DSSCs. It has since encouraged research into advanced TiO₂/graphene heterostructures, hierarchical nanocomposites, and ternary semiconductor systems to achieve even higher efficiencies and enhanced long-term stability (Lana et al., 2024; Rahman et al., 2023).

TiO₂ Photoanodes with a Modifier: Iron Oxide (Fe₂O₃)

The semiconductors investigated for the enhancement of DSSC performance include iron (III) oxide or hematite (Fe₂O₃), which has been the subject of much research due to its useful optical, electrical, and chemical properties. It is cheap, environmentally friendly, chemically stable, and abundant, and has a relatively small band gap of ~ 2.0–2.2 eV, which enables a high efficiency of light absorption over a large portion of the solar spectrum, which can absorb a greater fraction of the visible spectrum, which is a promising method to increase the light utilization efficiency of photoanodes (Rahman et al., 2023; Rani et al., 2019) compared to TiO₂ with ~3.2 eV. Fe₂O₃ is not only attractive for its light absorption properties. Hematite is chemically stable in water, has high corrosion resistance, is not poisonous, and has a natural abundance of sources, thus being one of the more sustainable semiconductors for photovoltaics. The positions of its conduction and valence bands are also suitable for a number of other semiconductor systems, enabling it to be paired to make heterojunctions, which can facilitate efficient charge separation and electron transfer. Therefore, Fe₂O₃ has been mainly explored as a TiO₂ photoanode modifier instead of being used as a photoanode material (Rahman et al., 2023).

It is possible that the incorporation of Fe₂O₃ in a TiO₂ photoanode can enhance the performance of the photoanode in several ways simultaneously. The smaller band gap allows the composite to have a photo response in the visible region, resulting in more of the available solar energy being captured. The Fe₂O₃/TiO₂ heterojunction also helps to separate the photogenerated electron–hole pairs by favoring the direction of electron transfer at the junction of Fe₂O₃ and TiO₂, reducing the rate of recombination, extending electron lifetime, and enhancing charge collection. Fe₂O₃ nanoparticles may also change the morphology of the surface of the TiO₂ films, providing more adsorption sites for the dye and

promoting more light scattering inside the photoanode, which leads to higher photocurrent generation (Lana et al., 2024; Rahman et al., 2023).

Pristine Fe₂O₃ is not without its own problems, though, which limit its use as a stand-alone photoanode material. It has low electron mobility, a short whole diffusion length (usually 2–4nm), poor electrical conductivity, and quickly recombines charge carriers. These properties limit charge transport and limit the PV performance possible from Fe₂O₃ alone. It also has a tendency to form nanoparticles during its synthesis process, reducing the surface area available for active use and reducing the contact between the two interfaces (nanoparticles and conductive substrates) and dye molecules. Therefore, Fe₂O₃ is more likely to be used in combination with other conductive materials, like graphene and TiO₂ (Lana et al., 2024; Munien et al., 2026; Rani et al., 2019), than on its own. The conclusion reached by parallel work is similar: such as the work done by Fe doped TiO₂ photoanodes and rGO hybridized TiO₂ photocatalysts, in the photocatalysis literature Fe doping reduces the band gap and enhances the visible light response and rGO doping enhances the charge separation, and in ternary Fe TiO₂/rGO system, it is found that the activity of the ternary system is better than that of the single Fe doped TiO₂ and rGO hybridized TiO₂ systems, which is similar to the situation in Fe₂O₃-graphene/TiO₂ photoanodes in DSSCs (Munien et al., 2026).

Thus, recent studies have turned to ternary Fe₂O₃-graphene/TiO₂ nanocomposites, with the mesoporous framework of TiO₂ providing a stable platform for dye adsorption and electron injection, graphene offering an ultra-fast pathway for electron transport and Fe₂O₃ extending the range of visible light absorption and increasing charge separation by heterojunction formation. These three factors can help to accelerate the electron transport kinetics, reduce the interfacial recombination, load more dye and enhance overall photovoltaic performance and this is why Fe₂O₃-graphene/TiO₂ ternary nanocomposites are one of the more promising photoanode systems to be used in next generation high efficiency DSSCs (Lana et al., 2024; Rahman et al., 2023).

Fe₂O₃-Graphene/TiO₂ Ternary Nanocomposite Photoanodes

The Synergistic Effect of Fe₂O₃, Graphene and TiO₂

The ternary Fe₂O₃/graphene/TiO₂ composites are truly a step forward in the design of a photoanode for DSSCs. They rely on the complementary properties of all three materials simultaneously, which helps in light harvesting, charge separation, electron transport and in enhancing the photovoltaic (PV) stability. The combination of Fe₂O₃, graphene and TiO₂ creates a multifunctional photoanode where each component plays its own role to enhance the

overall performance compared to the individual components (Lana et al., 2024; Rahman et al., 2023).

The basic structure of the photoanode is based on TiO₂. It has a mesoporous structure which is helpful in adsorption of dyes and it provides a large surface area that helps to inject an electron from excited dye molecules into its conduction band. It offers high chemical stability and favorable band edge positions, low toxicity, and is resistant to photocorrosion, but its relatively large band gap (~3.2 eV), relatively low electron mobility, and high recombination rate still limit the conversion efficiencies that can be achieved with TiO₂ alone (Hagfeldt & Vlachopoulos, 2018; Lana et al., 2024).

The primary role of graphene is to act as a fast electron transport material in the composite. Due to its excellent conductivity, high mobility of the carriers and large surface area, it creates a network of conducting paths within the TiO₂ matrix, providing low resistance pathways between the TiO₂ nanoparticles and the transparent conducting substrate. This reduces the charge transfer resistance and interfacial recombination. Graphene also enhances the mechanical stability of the photoanode, promotes dispersion of the nanoparticles and promotes strong bonding between the different components of the composite, increasing the stability of the devices and the photovoltaic performance. This effect of well optimized graphene loading on prominent enhancement of photocurrent generation and charge collection in DSSC has further been confirmed by the recent studies (Gusain et al., 2024; Lana et al., 2024; Rahman et al., 2023).

Fe₂O₃ can be used for both these purposes, shifting the optical response of the photoanode into the visible region. It has a much smaller band gap (2.0-2.2 eV) than TiO₂ does, and thus can absorb a much broader spectrum of the solar spectrum. When used in combination with TiO₂, it creates heterojunctions which spatially separate the charge carriers generated by the photons and minimize the recombination. It also changes the electronic structure of the composite, enhances the charge transfer at the interface, and enhances the light harvesting, especially in the visible light regime. Recent studies of iron modified TiO₂ have shown that it can simultaneously improve the charge separation and increase the spectrum absorption to achieve better PV performance (Lana et al., 2024; Rahman et al., 2023).

The Fe₂O₃-graphene/TiO₂ ternary nanocomposite is therefore scientifically motivated as a photoanode concept, but its photovoltaic superiority over binary systems remains to be demonstrated experimentally. When illuminated, dye molecules absorb photons and put excited electrons into the conduction band of TiO₂. These electrons are not trapped in the TiO₂ network but are promptly transferred to the graphene structure that has a highly conductive framework and efficiently transports

them to the FTO substrate and external circuit. Meanwhile, the Fe₂O₃/TiO₂ heterojunction ensures that charge carriers flow in the correct direction, and reduces back electron transfer. The resulting combination of enhanced visible light absorption, improved electron transport, suppressed electron/hole recombination and improved interfacial contact increases the short circuit current density, the electron lifetime, the fill factor and overall power conversion efficiency of the device (Hagfeldt & Vlachopoulos, 2018; Lana et al., 2024; Rahman et al., 2023).

The synergistic effects are also sharpened by the progress of nanocomposite engineering, such as the design of good interfaces, control of morphology, and the assembling of nanostructures. New techniques like hydrothermal synthesis, sol gel processing, solvothermal growth, electrospinning and in situ reduction of graphene oxide have enabled significantly more control over the dispersion and interfacial bonding of the nanoparticles, resulting in ternary photoanodes that exhibit more uniform structure, improved conductivity, and greater stability than earlier binary systems (Lana et al., 2024; Rahman et al., 2023).

Combining TiO₂ as the primary electron-accepting semiconductor, graphene as a highly conductive transport network, and Fe₂O₃ as a visible light active heterojunction modifier appears to be a viable strategy to overcome the limitations of conventional TiO₂ photoanodes. The Fe₂O₃-graphene/TiO₂ ternary nanocomposite is therefore scientifically motivated as a photoanode concept, but its photovoltaic superiority over binary systems remains to be demonstrated experimentally (Lana et al., 2024; Rahman et al., 2023).

Synthesis Strategies for Fe₂O₃-graphene/TiO₂ Ternary Nanocomposites

The Fe₂O₃/graphene/TiO₂ photoanode is highly sensitive to the preparation method. Morphology and crystallinity are not the only features affected by synthesis route: pores, dispersibility in graphene, particle size, charge transfer pathways, and crystallographic defect are also affected. Thus, an appropriate synthesis strategy is essential to realize an efficient, high surface area, high conductivity, and stable photoanode.

Hydrothermal Method

One of the most widely used routes for the preparation of Fe₂O₃-graphene/TiO₂ nanocomposites is the hydrothermal method, which has the advantage of being simple and achieving well crystallized and well controlled nanostructures. Precursor solutions with titanium, iron and graphene oxide are put into a Teflon lined stainless steel autoclave and heated under high temperature and pressure. During the reaction, the graphene oxide is partially or completely reduced to form rGO, and the TiO₂ and Fe₂O₃ nanoparticles form and

grow directly on the graphene surface, leading to a close interfacial contact (Gusain et al., 2024; Purabgola et al., 2022).

The method has advantages such as uniform distribution of nanoparticles, high crystallinity, good interface bonding, and controlled shapes of nanoparticles and could also construct hierarchical porous structures with high surface area of the porous structure for dye adsorption and fast electron transport. The drawbacks include the need for special autoclaves, relatively long reaction time, and the careful control of reaction time, precursor concentration, temperature and pressure for reproducible results. Despite this, it is still the most commonly reported method for metal oxide nanocomposites with graphene, as it allows for good control of the morphology and reduces the graphene oxide during the composite formation process (Lana et al., 2024; Purabgola et al., 2022).

Sol-Gel Method

Another method that is widely used to produce ternary Fe₂O₃-graphene/TiO₂ nanocomposites is the sol gel process. Metal alkoxide precursors are hydrolyzed and condensed into a uniform sol, which over time turns into a gel network containing uniform graphene sheets and iron species. Drying and calcining this gel then produces a crystalline composite photoanode in which all the components are in intimate contact (Lana et al., 2024; Rahman et al., 2023).

Its greatest advantage is its compositional homogeneity at the molecular level and the fine control it offers over Fe₂O₃ loading, graphene content, particle size, and film composition. It also applies comparatively low processing temperatures, which helps avoid the damage of the graphene structure and results in the uniform dispersion of iron oxide in the TiO₂ matrix. It has drawbacks of relatively long processing time, shrinkage during drying and a possible agglomeration of nanoparticles during calcination. Recent reviews have confirmed that sol gel route represents one of the most effective methods to get uniform TiO₂/graphene composites (Lana et al., 2024).

Solvothermal Method

The solvothermal technique is similar to the hydrothermal process, except that water is replaced with organic solvents. Organic media are used to obtain better control over solubility of the precursors, crystal growth and shape of the particles, which often result in highly crystalline nanoparticles with a narrow size distribution. This is particularly convenient for the synthesis of complicated heterostructures and the control of Fe₂O₃ and TiO₂ nucleation on the surface of graphene (Gusain et al., 2024; Lana et al., 2024).

It offers improved crystallinity and greater flexibility in the control of morphology compared to hydrothermal

synthesis, but generally requires the use of an expensive organic solvent, recovery of solvent and more rigorous safety requirements to make large-scale production more difficult (Rahman et al., 2023).

Microwave-Assisted Synthesis

Microwave-assisted synthesis has become more popular as microwave irradiation can heat up the reaction medium quickly and uniformly over all the volume of the reaction vessel, which accelerates the nucleation and crystal growth process and reduces the reaction time from hours to minutes (Rahman et al., 2023).

This fast and even heating generally suppresses the tendency for nanoparticles to agglomerate and frequently leads to much dispersed TiO₂ and Fe₂O₃ nanoparticles on the graphene sheets, as well as better crystallinity and conductivity in the final composite. The main disadvantage is the requirement for specialized equipment, making it difficult to scale up for industrial production. It is still regarded as a promising method for the quick preparation of graphene based semiconductor nanocomposites with controlled morphology in recent reviews (Lana et al., 2024).

Electrospinning

The 1-D interconnected porous photoanodes fabricated by electrospinning have been attractive and promising. The precursor solutions of TiO₂, iron salts and graphene oxide are broken down under high electric field to form continuous composite nanofibers and the nanofibers are transformed to crystalline Fe₂O₃-graphene/TiO₂ fibers by calcination (Anish Madhavan et al., 2012; Lana et al., 2024).

The engineered nanofibrous structure eliminates direct electron transport pathways and provides for greater electrolyte penetration, dye loading and grain boundary resistance than do nanoparticle based photoanodes. Despite this, proper control of fiber diameter, calcination conditions and the distribution of graphene are still necessary to obtain a good PV performance (Lana et al., 2024).

Ultrasonic (Sonication) Assisted Assembly

In general, sonication is carried out as a preliminary dispersion process before hydrothermal or sol gel processing. It is found that ultrasonic exfoliation can exfoliate the graphene oxide sheets and dispersion of TiO₂ and Fe₂O₃ nanoparticles is effective without agglomeration, thus improving the interfacial contact in the composite (Lana et al., 2024; Purabgola et al., 2022). Sonication alone is insufficient to obtain a complete nanocomposite, but it is highly effective at dispersing graphene and distributing particles, and therefore can be used as a valuable auxiliary step in the fabrication of composites. It is also very easy to use and is available at

low cost and simplicity making it desirable for laboratory scale synthesis (Rahman et al., 2023).

Characterization Techniques for Fe₂O₃-graphene/TiO₂ Ternary Photoanodes

A wide range of characterization tools spanning crystal structure, morphology, chemical composition, optical properties, surface properties and charge transfer properties are needed to understand the relationship between the properties of Fe₂O₃-graphene/TiO₂ ternary nanocomposites and their photovoltaic performance. These methods are combined to provide a comprehensive understanding of the composite formation, structure, chemical interactions and final performance of a DSSC (Lana et al., 2024; Rahman et al., 2023).

X-ray Diffraction (XRD)

One of the most widely used methods to determine the crystal structure, phase composition, crystallite size and crystallinity of these nanocomposites is XRD. The anatase and rutile phase of TiO₂ were identified from the diffraction patterns, and no peaks of any impurities were observed, which is considered to imply that the composite was not formed with any unwanted secondary phases. One of the typical diffraction peaks of graphene or rGO is often weak in graphene composites due to its low concentration and partial exfoliation. XRD can be used to determine the crystalline phases present and, using the Scherrer equation, provide information on the crystallite size, the crystallinity and phase composition. Changes in peak positions, intensities and/or peak broadening can be indicative of composites formation and potential structural interactions with characteristic reflections from TiO₂ and α -Fe₂O₃. In order to use XRD data to interpret the content of rGO, complementary techniques such as Raman spectroscopy, XPS and electron microscopy are used. In general, higher crystallinity is beneficial for charge transport and minimizes defect related recombination, but the net effect on photovoltaic properties of the composites remains dependent upon the morphology, interface structure and electronic properties (Ali et al., 2022; Lana et al., 2024).

Scanning Electron Microscopy (SEM)

The surface morphology and microstructure of the photoanode films can be investigated by SEM, including the particle distribution, surface texture, pore structure, grain connectivity and roughness, and cross-sectional SEM may be used to provide an estimation of the film thickness. The morphological characteristics affect the adsorption of dyes, penetration of electrolytes, electron transport and contact of the interfaces.

The Fe₂O₃ nanoparticles and graphene sheets are evenly distributed in the TiO₂ matrix, indicating high dispersion and integration of the components in the composite. Agglomeration or uneven distribution of graphene,

however, can reduce the available surface area, reduce the ability of the electrolyte and dye to interact, and reduce the ability of the dye to charge transport, which can negatively affect the photovoltaic performance.

Transmission Electron Microscopy (TEM)

The TEM provides high-resolution images of the internal structure of the nanocomposite, allowing researchers to see how the TiO₂ nanoparticles are associated with the graphene sheets, and how the Fe₂O₃ nanoparticles are distributed in the composite. When the image is taken by high resolution TEM (HRTEM), the lattice fringes which are associated with certain crystallographic planes can be resolved and the spatial correlation of crystalline phases can be determined. The presence of lattice fringes close to the graphene network, in both TiO₂ and Fe₂O₃, is considered as proof of intimate interfacial contact within the ternary composite contact that could contribute to charge separation and electron transfer, which needs to be further confirmed by other electrical and spectroscopic measurements (Lana et al., 2024; Sierra, 2019).

Raman Spectroscopy

Raman spectroscopy can be used especially for identification of graphene-based carbon materials, and determination of their structural quality. The D band (around 1350 cm⁻¹) is due to disorder and defects of the sp² network, and the G band (around 1580 cm⁻¹) is due to the in plane vibrational mode of sp² bonded carbon. The value of the intensity ratio of these two bands (I_D/I_G) is indicative of the degree of structural disorder and can monitor structural change upon the reduction of GO or the formation of the composite, but it should be used with care as it is not a direct and simple measure of the defect density; other structural factors can also affect this ratio. Raman spectroscopy can also detect characteristic vibrations of TiO₂ and α -Fe₂O₃, and changes in their vibrational environments can also be monitored. In conjunction with XRD, XPS and electron microscopy, it provides useful supporting data to understand the formation and interactions within the ternary composite. (Rahman et al., 2023).

X-ray Photoelectron Spectroscopy (XPS)

XPS determines the elemental composition and chemical states of the elements at or near the nanocomposite's surface. The oxidation states of the Ti, Fe, O and C elements and the changes in their chemical environments can be determined from the analysis of the Ti 2p, Fe 2p, O 1s and C 1s core level spectra. These changes in binding energy, new peak components, and changes in the relative contribution of different chemical states may indicate the interactions at interfaces between TiO₂, α -Fe₂O₃, and graphene. For some of these shifts, if supported by appropriate peak fitting and supporting characterization, these shifts can signify, for example,

bonding or electronic interaction between the interfaces, such as Ti–O–Fe bonds, or the presence of carbon containing species, that might lead to improved charge separation and electron transfer in the ternary photoanode (Krishna & Philip, 2022; Lana et al., 2024).

Fourier Transform Infrared Spectroscopy (FTIR)

Chemical functional groups present in the nanocomposite and changes related to the reduction of graphene oxide are identified using FTIR. The decrease in the absorption intensity associated with the hydroxyl, epoxy and carboxyl functional group oxygen containing species is consistent with the reduction of graphene oxide to rGO. FTIR bands also may contain characteristic metal–oxygen bands for Ti–O and Fe–O, and changes in the position or intensity of these bands may indicate interactions between the different phases of the composite.

UV–Visible Spectroscopy

The optical absorption of the photoanodes is measured using UV–Vis spectroscopy. The presence of α -Fe₂O₃, whose band gap (≈ 2.0 – 2.2 eV) is narrower than that of TiO₂ (≈ 3.2 eV), extends the optical absorption of the composite into the visible region. A higher visible light absorption in the Fe₂O₃-graphene/TiO₂ composites indicates that they can potentially utilize a greater proportion of the solar spectrum, but this alone does not necessarily make them more efficient at PV conversion; the optical absorption can be used to calculate the different energies of the composites using an appropriate transition model and result in the Tauc plots, which can then be compared to each other (Hajakbari et al., 2010; Lana et al., 2024).

Photoluminescence (PL) Spectroscopy

PL spectroscopy provides information of the recombination of the charge carriers thermally generated by the photons. The reduction of PL emission intensity compared to a reference material usually indicates reduced radiative recombination and improved charge separation. In several reports, composites of Fe₂O₃ with graphene were prepared on TiO₂ and a decrease in PL intensity was observed relative to its counterpart, pure TiO₂, indicating that the incorporation of Fe₂O₃ and graphene influences separation and transport of charge carriers within the compound (Lana et al., 2024; Rahman et al., 2023).

Brunauer-Emmett-Teller (BET) Surface Area Analysis

The specific surface area, pore volume and pore size characteristics of the photoanode materials are measured by BET analysis. The porous structure of Fe₂O₃-graphene/TiO₂ composites can affect both dye loading and charge transport, with a higher specific surface area providing more adsorption sites for dyes and enhance the

interaction between the electrolyte and the photoanode. However, a larger surface area does not necessarily mean a higher PV performance, as other factors such as pore connectivity, particle aggregation and film thickness, electron transport and recombination also come into play. The dye loading and the morphological data combined with the photovoltaic parameters are needed to assess the appropriateness of a ternary photoanode for DSSC application in conjunction with BET results (Brunauer et al., 1938; Lana et al., 2024).

Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful technique for revealing the charge transfer and recombination characteristics of a DSSC, providing data on charge transfer resistance, transport resistance, recombination resistance and electron lifetime at different interfaces of the cells. Changes in charge transport kinetics and interfacial behavior can be tracked by Nyquist plots and Bode plots; a lower charge transfer resistance is representative of more favorable charge transport behavior, and a longer electron lifetime indicates less recombination behavior. Several reported Fe₂O₃-graphene/TiO₂ photoanodes show reduced interfacial resistance compared with pristine TiO₂, which may stem from the conductive graphene network and the interfacial interaction between Fe₂O₃ and TiO₂ though these effects depend strongly on composition, morphology, interfacial contact and the relative loading of each material, and should be read alongside complementary photovoltaic and spectroscopic data (Lana et al., 2024; Pospisil et al., 2023; Rahman et al., 2023).

Recent Advances in Fe₂O₃-graphene/TiO₂ Based Photoanodes for Dye-Sensitized Solar Cells

New developments in Fe₂O₃-graphene/TiO₂ based photoanodes for DSSCs. Fe₂O₃-graphene/TiO₂ based photoanodes for DSSC have experienced a steady progress in the past few years. Most of the recent studies focus on addressing the drawbacks of pristine TiO₂, such as limited electron mobility, slow charge recombination and its wide band gap, by folding graphene and iron oxide to form ternary nanocomposites. New developments in the field of interface design and synthesis technique, as well as in nanostructure engineering have led to improvements in light harvesting, electron transport and photovoltaic efficiencies (Lana et al., 2024; Rahman et al., 2023; Tayari et al., 2025).

A notable direction is the departure from random mixing of nanocomposites to carefully designed heterostructures with controlled interfaces. The combination of layered TiO₂/rGO photoanodes, hierarchical porous architectures and Fe modified TiO₂ systems have all demonstrated improved performance, which resulted from a combination of dye loading, extended visible light absorption and promoted electron extraction. Recent

research has revealed that graphene is not only conductive but also changes the morphology of TiO₂ network, which reduces the charge transfer resistance and inhibits recombination. One of the other significant developments is the more careful control of the amount of Iron that is put in the TiO₂ photoanode. Instead of adding more Fe₂O₃, recent research demonstrates that a moderate amount of iron can be incorporated into the material to narrow the optical energy gap without sacrificing the efficient electron transport, which is optimized by a controlled moderate amount of iron that allows good absorption of visible light and favors charge separation through heterojunction formation, while too high a concentration of iron introduces recombination centers, which are detrimental to the performance. This emphasizes the significance of the composition optimization process when being fabricated (Lana et al., 2024; Rahman et al., 2023).

There has also been a recent focus on the TiO₂ graphene interface itself in the fabrication. The strategy of placing reduced graphene oxide at an optimized location in the TiO₂ film results in superior dye adsorption, light utilization, electron transport and recombination losses compared to a TiO₂ film. Engineered structures show efficiencies of over 80% compared to conventional P25 based photoanodes, highlighting that interface engineering is much more important than simply incorporating more graphene (Lana et al., 2024; Yang et al., 2010).

The ways of incorporating graphene have evolved too. More recent methods to the physical mixing of graphene with TiO₂-nanoparticles are based on in situ reduction of graphene oxide, hydrothermal growth and layer by layer assembly of graphene sheets and semiconductor particles, to create a closer contact between them. The methods create conducting networks of continuous sheets, which significantly reduce electron diffusion pathways and enhance electron collection efficiency, along with controlled loading of graphene; the sheet aggregation during loading is mitigated to prevent additional recombination sites from undermining the conductive properties of graphene (Lana et al., 2024; Purabgola et al., 2022).

In addition to synthesis itself, researchers are now turning to more sophisticated characterization techniques like EIS, intensity modulated photovoltage spectroscopy (IMVS), transient photocurrent measurements, and photoluminescence spectroscopy, to make the case that the structure of the nanocomposite directly translates to photovoltaic functionality. Several studies have found that the addition of graphene, Fe₂O₃ to TiO₂ has resulted in a lower resistance of charge transfer, longer lifetime of electrons, improved charge separation, or higher photocurrent, depending on the size of the effects and direction of these effects (decrease or increase) and depend on composition, loading ratio, morphology,

synthesis route, and the level of interfacial architecture. However, there is relatively little direct evidence in the literature, derived from fully integrated Fe₂O₃-graphene/TiO₂ ternary DSSC photoanodes (Lana et al., 2024; Rahman et al., 2023).

Nevertheless, few studies examine a fully integrated Fe₂O₃-graphene/TiO₂ ternary nanocomposite specifically designed for a DSSC most of the recent literature is based on binary TiO₂/graphene systems or iron modified TiO₂, but with graphene not included in the same system. This suggests that ternary Fe₂O₃-graphene/TiO₂ photoanodes are still in their infancy and offer considerable potential. Optimized heterojunction design, scalable synthesis, long term operational stability, and a more systematic investigation of the use of appropriate amount of Fe₂O₃ and graphene for the optimum photovoltaic performance in a reliable manner are suggested as future research areas (Lana et al., 2024; Rahman et al., 2023).

Photovoltaic Performance of Fe₂O₃-and Graphene-Modified TiO₂ Photoanodes

Recent studies demonstrate that significant changes in the performance of a DSSC can be obtained by modifying the TiO₂ photoanode with Fe₂O₃ or graphene derived materials. The optical response of TiO₂ can be extended into the visible region and the interfacial charge transfer behavior can be changed by Fe₂O₃; graphene or rGO can provide conductive pathways and may influence the adsorption of dyes and the transport of electrons. However, the vast majority of literature focuses on the individual systems of Fe₂O₃/TiO₂ and graphene/TiO₂; a few studies have investigated the combination of Fe₂O₃ and graphene into a single photoanode of TiO₂.

Da Cunha et al. (Da Cunha et al., 2026) recently examined TiO₂-Fe₂O₃ photoanodes with 10, 20 and 30 wt% Fe₂O₃, sensitized with natural dyes. For cells sensitized with Alstroemeria dye, the best-performing composition 20 wt% Fe₂O₃ gave a J_{sc} of 3.91 mA cm⁻², Voc of 0.60 V, FF of 0.43 and PCE of 6.33%, versus just 2.04 mA cm⁻², 0.39 V, 0.29 and 1.74% for the corresponding plain TiO₂ photoanode. Efficiency dropped back to 5.74% at 30 wt% Fe₂O₃, showing that piling on more Fe₂O₃ does not necessarily help the authors linked the 20 wt% optimum to a balance between light absorption, charge transport and photoanode morphology (Da Cunha et al., 2026).

Equally promising results have been achieved for the use of graphene-derived modification. Peiris et al. (Peiris et al., 2021) fabricated an rGO/TiO₂ photoanode with electrophoretic deposition and at the optimum rGO content, the fabricated DSSC obtained the maximum J_{sc} of 18.37 mA cm⁻², Voc of 0.61 V, FF of 52.1% and PCE of 6.52%, which was attributed to the improved dye absorption, light harvesting and charge transport capability of rGO on TiO₂ photoanode.

Likewise, Dang et al. (Dang et al., 2021) prepared TiO₂/rGO nanocomposites by hydrothermal co precipitation method and constructed DSSC photoanodes by screen printing technique. The highest Jsc and PCE of 17.65 mA cm⁻² and 7.46% respectively were obtained for the best performing composition 0.6 wt% rGO, which also had the longest electron lifetime and most favorable electrochemical behavior among the compositions tested. Voc across the compositions varied from 0.67 to 0.73 V, and FF varied from 0.59 to 0.67, but as the source does not specify which of the two parameters goes with which optimum 0.6 wt% composition, the two are marked as not being uniquely assigned to each other in Table 1, rather than being guessed at.

These studies suggest that Fe₂O₃ and graphene derivatives can be used independently to enhance the PV response of TiO₂-based DSSC with different mechanisms and different optimum loadings. Fe₂O₃ will predominantly cause optical and interfacial electronic changes and graphene derivatives will introduce conductive pathways while at the same time enhancing the use of dye and electron transport. Importantly, in both, the best loading is not the one where Fe₂O₃ or rGO is used most. The results provide an excellent foundation to investigate the combination of Fe₂O₃ and graphene in TiO₂ and to systematically optimize the composition and interfacial structure of ternary photoanodes.

Table 1: Representative Photovoltaic Performance of Fe₂O₃ and Graphene Modified TiO₂ DSSC Photoanodes

Author/Year	Photoanode	Modification / optimum loading	Jsc (mA cm ⁻²)	Voc (V)	FF	PCE (%)	Key observation
(Da Cunha et al., 2026)	TiO ₂ /Fe ₂ O ₃	20 wt% Fe ₂ O ₃ ; Alstroemeria dye	3.91	0.60	0.43	6.33	Optimum Fe ₂ O ₃ loading; excessive loading reduced PCE
(Peiris et al., 2021)	rGO–TiO ₂	Optimum proportion rGO	18.37	0.61	0.52	6.52	rGO enhanced dye absorption, light harvesting and photocurrent
(Dang et al., 2021)	TiO ₂ /rGO	0.6 wt% rGO	17.65	NR	NR	7.46	Optimum rGO loading produced the highest Jsc, electron lifetime, and PCE
(Yang et al., 2010)	rGO/TiO ₂ on ITO	Molecular assembly and electrophoretic deposition; N719 dye	6.67	0.56	0.45	1.68	Titanium butoxide functionalisation of GO strengthened the TiO ₂ –graphene interface and raised conductivity above pristine TiO ₂
(Anish Madhavan et al., 2012)	Graphene/TiO ₂ nanofibers	Graphene incorporated into electrospun TiO ₂ nanofibres	16.2	0.71	0.66	7.6	Outperformed the pristine TiO ₂ nanofibre reference (13.9 mA cm ⁻² , 0.71 V, 0.63, 6.3%)
(Tang et al., 2018)	rGO/TiO ₂ dual-layer	4 wt% rGO in the work layer plus an rGO–TiO ₂ scattering layer	11.8	NR	NR	NR	Optimising RGO functional groups and mass fraction separately in the work and scattering layers gave roughly 20% enhancement from the work layer alone
(Singh et al., 2022)	TiO ₂ –rGO	GO reduced at 150 °C and blended into mesoporous TiO ₂	16.90	0.739	0.705	8.80	Reduction temperature controlled residual oxygen content; roughly 23% PCE gain over unmodified TiO ₂
(Makal & Das, 2021)	rGO/TiO ₂ -B nanowires	8 wt% rGO laminated onto 1D TiO ₂ -bronze nanowires	10.41	0.71	0.67	4.95	IPCE peaked at 51% for 8 wt% RGO; loadings above 8 wt% reduced conversion efficiency

Comparative Analysis of Previous Reviews

Table 2: Structured Comparison of Previous Reviews and Related Contributions with the Scope and Contribution of the Present Review

Authors/Year	Main Focus	Scope/Key Contribution	Limitation	Distinction From Present Review
(Hatib et al., 2024)	TiO ₂ /rGO photoanodes for DSSCs	Developed and characterized layered TiO ₂ /rGO photoanodes with improved electron transport and reduced recombination	Considered only binary TiO ₂ /rGO systems; Fe ₂ O ₃ was not incorporated	This review evaluates the synergistic integration of Fe ₂ O ₃ , graphene and TiO ₂ in ternary photoanodes and consolidates recent developments
(Bella et al., 2015)	Aqueous dye-sensitized solar cells	Reviewed developments in DSSC materials, device architectures and commercialization prospects, with emphasis on aqueous electrolytes	Broad DSSC coverage with limited emphasis on ternary photoanode engineering	The present review provides an in-depth treatment of ternary Fe ₂ O ₃ –graphene/TiO ₂ photoanodes specifically
(Shaik et al., 2024)	Graphene/TiO ₂ nanocomposites	Reviewed synthesis routes and applications of TiO ₂ /graphene nanocomposites in energy and environmental devices	Focused mainly on photocatalysis; limited discussion of DSSC photoanodes	This review is directed at DSSC photoanodes and at Fe ₂ O ₃ incorporation within them

Authors/Year	Main Focus	Scope/Key Contribution	Limitation	Distinction From Present Review
(Purabgola et al., 2022)	Graphene-based TiO ₂ composites	Reviewed synthesis, properties and applications of graphene–TiO ₂ nanocomposites for photocatalysis and environmental remediation	Limited discussion of Fe ₂ O ₃ modification and of DSSC photoanodes	The present review focuses on Fe ₂ O ₃ –graphene/TiO ₂ ternary photoanodes for DSSCs and their charge-transfer mechanisms
(Rahman et al., 2023)	DSSC constituents and efficiency enhancement	Comprehensive review of DSSC components, materials, efficiency-enhancement strategies and future prospects	Treated DSSCs broadly without detailed emphasis on Fe ₂ O ₃ –graphene/TiO ₂ ternary photoanodes	This review analyses Fe ₂ O ₃ –incorporated graphene/TiO ₂ photoanodes in depth, covering synthesis, characterization and recent advances
(Lana et al., 2024)	One-dimensional TiO ₂ nanocomposite photoanodes	Reviewed one-dimensional TiO ₂ nanostructures, electron transport behavior and photovoltaic performance in DSSCs	Concentrated on one-dimensional TiO ₂ systems, with limited discussion of graphene–Fe ₂ O ₃ ternary architectures	The present review examines ternary Fe ₂ O ₃ –graphene/TiO ₂ photoanodes and the synergistic interaction among the three components
(O'regan & Grätzel, 1991)	Foundational DSSC concept	Introduced the dye-sensitized solar cell based on nanocrystalline TiO ₂ and established its operating principle	Predates nanocomposite photoanodes and graphene-based materials entirely	The present review addresses modern ternary photoanode architectures developed over the past decade
(Botsa, 2025)	rGO-assisted TiO ₂ –Fe ₂ O ₃ ternary nanocomposite	Demonstrated an rGO-assisted TiO ₂ –Fe ₂ O ₃ ternary nanocomposite and characterized its visible-light-driven activity, establishing that the three phases can be combined with functional benefit	Applied the ternary composite to photocatalytic degradation of nitrobenzene and dye pollutants rather than to photovoltaic devices; no DSSC photovoltaic parameters reported	The present review transfers this ternary concept to the DSSC photoanode context and analyses it against photovoltaic rather than photocatalytic performance metrics
(Debnath et al., 2024)	Principles, materials and mechanism of DSSCs	Comprehensive review of DSSC fundamentals including photoanodes, sensitizers, electrolytes, counter electrodes and efficiency and stability strategies	Provides a broad overview without in-depth treatment of Fe ₂ O ₃ –graphene/TiO ₂ ternary photoanodes	The present review is dedicated exclusively to ternary Fe ₂ O ₃ –graphene/TiO ₂ photoanodes and analyses their synthesis, characterization, mechanisms, performance and research gaps
(Odebunmi et al., 2026)	Ni- and GO-modified TiO ₂ photoanodes	Reviewed the synergistic roles of nickel and graphene oxide as modifiers of TiO ₂ photoanodes, covering synthesis, characterization and photovoltaic performance	Centered on Ni–GO modification; Fe ₂ O ₃ was not considered as a modifying component	The present review centers on Fe ₂ O ₃ as the visible-light-active modifier paired with graphene, offering a complementary perspective on ternary TiO ₂ photoanode design
(Olaniyi et al., 2026)	Iron oxide–graphene–TiO ₂ multifunctional nanostructures	A contemporaneous review of synthesis and characterization of iron oxide–graphene–TiO ₂ nanocomposites and their photoanode performance, closely aligned with the present topic	As a parallel, independently produced review, it does not include a structured comparative-review analysis, research-gap mapping, or the synthesis-strategy taxonomy developed here	The present review complements it with an independent literature synthesis, an explicit comparison against prior reviews (this table), and a dedicated research-gaps and future-perspectives framework
(Korir et al., 2024)	Current status of DSSCs	Reviewed the status of DSSC technology across sensitizers, photoanodes, electrolytes and counter electrodes with emphasis on sustainability	Surveys the technology as a whole; individual composite photoanode architectures are not analyzed in mechanistic detail	The present review restricts its scope to one photoanode architecture and examines its composition–structure–performance relationships in detail
(Roza et al., 2025)	Metal oxide–carbon heterostructure photoanodes	Reviewed metal oxide/nanostructured carbonaceous material heterostructures as DSSC photoanodes, covering physical and chemical preparation techniques and resulting properties	Addresses metal oxide–carbon pairings generally; the specific case of a visible-light-active iron oxide combined with graphene in TiO ₂ is not isolated	The present review treats one specific ternary combination and evaluates the distinct functional contribution of each of the three components
(Khairudin et al., 2026)	Metal oxide modification for	Reviewed doping, compositing and coating as the three principal routes for modifying metal oxide	Organized by modification method across many metal oxides rather than by a	The present review is organized around a single ternary architecture and

Authors/Year	Main Focus	Scope/Key Contribution	Limitation	Distinction From Present Review
	DSSC photoanodes	photoanodes, relating efficiency to charge-transfer resistance from EIS data	specific composite system; Fe ₂ O ₃ –graphene/TiO ₂ is not treated as a distinct architecture	integrates synthesis, characterization and photovoltaic evidence for it
(Muchuweni et al., 2025)	rGO-based composites as DSSC electrode alternatives	Reviewed advances between 2020 and 2024 in TiO ₂ -free photoanodes and Pt-free counter electrodes based on rGO combined with metal oxides, chalcogenides and perovskites	Directed toward replacing TiO ₂ and Pt rather than toward improving TiO ₂ -based photoanodes; iron oxide is not a principal focus	The present review retains TiO ₂ as the host semiconductor and examines how Fe ₂ O ₃ and graphene together address its specific optical and transport limitations
(Zhou et al., 2025)	Key materials and fabrication strategies for high-performance DSSCs	Comprehensive comparison of photoanode, dye, electrolyte and interface materials for high-efficiency DSSCs	General device-level materials review; no dedicated treatment of Fe ₂ O ₃ or ternary photoanode composites	The present review is confined to one photoanode composite family and treats composition–interface–transport relationships in depth
(Srivastava et al., 2025)	One-dimensional TiO ₂ photoanodes	Focused review of nanorod, nanowire and nanotube TiO ₂ morphologies for DSSC photoanodes	Restricted to TiO ₂ morphology; does not address graphene or Fe ₂ O ₃ modification	The present review addresses compositional modification of TiO ₂ by graphene and Fe ₂ O ₃ rather than morphology alone
(Qamar & Ela, 2024)	DSSC principles, materials and working mechanism	Comprehensive review of photoanode, sensitizer, electrolyte, counter-electrode and solid-state electrolyte materials for long-term stable DSSCs	Broad materials-level coverage across all DSSC components; no dedicated treatment of Fe ₂ O ₃ or ternary photoanode composites	The present review is confined to one photoanode architecture and analyses its composition–interface–transport relationships in depth

Discussion of Comparative Studies

The reviews summarized in Table 2 show that considerable attention has already gone into improving DSSC performance through TiO₂ modification, graphene-based conductive networks, heterojunction formation, and advanced photoanode architectures. Hatib et al. (Hatib et al., 2024), for instance, focused on TiO₂/rGO photoanodes and the role graphene-derived conductive pathways play in improving electron transport and reducing recombination. Purabgola et al. (Purabgola et al., 2022) Similarly reviewed graphene TiO₂ nanocomposites and their use in photocatalytic and photovoltaic systems. Useful as these reviews are for understanding graphene's contribution to TiO₂ based photoanodes, neither centers its discussion on combining Fe₂O₃ and graphene within TiO₂ for DSSCs specifically. Broader DSSC reviews Bella et al. (Bella et al., 2015), Rahman et al. (Rahman et al., 2023) cover DSSC materials, device architectures, operating principles, efficiency-enhancement strategies and stability considerations comprehensively, but their wide scope leaves little room to dig deeply into any one ternary photoanode architecture. Other reviews, such as Shaik et al. (Shaik et al., 2024) and Lana et al. (Lana et al., 2024), offer more focused looks at graphene/TiO₂ nanocomposites or nanostructured TiO₂ photoanodes respectively, but neither builds a dedicated framework for weighing the combined roles of Fe₂O₃, graphene and TiO₂ together. Odebunmi et al. (Odebunmi et al., 2026) have written a review of nickel, not iron oxide, but instead of graphene oxide as co modifier, while Olaniyi et al. (Olaniyi et al., 2026) have written a review of

essentially the same ternary system, iron oxide, graphene and TiO₂, in a contemporary review that is independent of the other.

The state of the art of DSSC technology for all four major components is summarized by Korir et al. (Korir et al., 2024) and the metal oxide–carbon heterostructures are handled in general by Roza et al. (Roza et al., 2025), excluding the situation where the second oxide component is also visible-light-active. Khairudin et al. (Khairudin et al., 2026) categorized modification by the photoanodes by modification methodology, such as doping, compositing and coating; efficiency vs. charge-transfer resistance, deduced from EIS, methodology that is structurally similar, but sorted by methodological approach instead of ordering by type of material system. Muchuweni et al. (Muchuweni et al., 2025) reviewed rGO-based composites published between 2020 and 2024, with a focus on replacing TiO₂ in photoanodes and Pt in counter electrodes, as opposed to enhancing TiO₂-based photoanodes as in the present review. A note should definitely be included for the work by Botsa (Botsa, 2025) who showed a ternary TiO₂–Fe₂O₃ nanocomposite with the aid of rGO, with the three-phases also being combined for function where they are photocatalytic degradation of nitrobenzene and dye pollutants, prominently, but not for the PV field. The study is therefore the most comprehensive existing evidence indicating the chemical viability of the ternary combination and at the same time showing why its photovoltaic potential has not been tested yet: the composite is found in the literature of photocatalysis but

not in the literature of DSSC photoanode design, where a photovoltaic parameter has been reported.

This comparison highlights an obvious missing link in the review literature. Individual effects of TiO₂, graphene, rGO and Fe₂O₃ to the performance of the photoanode have been studied separately, but there has been no focused review that combines all three into a single Fe₂O₃–graphene/TiO₂ framework. This review aims to fill this gap by collecting recent literature on the synthesis process, the structural and optical characterization, charge transfer mechanisms, the PV performance, optimization of loading of Fe₂O₃ and of graphene, the issues of ternary photoanode design. The novelty of this review is that it focuses on the relationship between the composition, the interfacial structure, charge transport and photovoltaic performance. It isn't about graphene or Fe₂O₃ alone, but about understanding how they may be combined within the TiO₂ based photoanodes and when this combination will be beneficial. This method also reveals a number of unanswered questions that should be highlighted, such as: In the few directly comparable ternary DSSC studies that exist, photovoltaic parameters are not reported

consistently; the optimization of loading of the components; issues involving recombination at the interfaces; morphological control; scale up; and long-term device stability.

Research Gaps, Challenges and Future Perspectives

Research Gaps

Though graphene, TiO₂ and Fe₂O₃-based photoanodes have been successfully developed for DSSC, significant challenges still exist in the development of fully integrated Fe₂O₃–graphene/TiO₂ ternary photoanodes. Although most of the studies reported in this review still concentrate on the binary TiO₂/graphene, TiO₂/rGO or Fe₂O₃/TiO₂ systems, and systematic studies of Fe₂O₃ and graphene in the same TiO₂ photoanode are still less common. The most obvious finding of this review is the scarcity of systematic studies on fully integrated Fe₂O₃–graphene/TiO₂ ternary photoanodes for DSSCs. Consequently, it remains unclear to date how the three components can complement each other in light harvesting, electron transport and charge separation. Table 3 classifies the studies discussed in this review by the type of evidence they provide.

Table 3: Classification of the primary studies compiled in Table 1, together with Botsa (2025), by type of evidence relevant to the Fe₂O₃–graphene/TiO₂ DSSC photoanode

Type of evidence	Studies	System investigated		Relevance to the ternary photoanode
Direct ternary DSSC evidence	None identified	Fe ₂ O ₃ –graphene/TiO ₂ photoanode in a DSSC		Not yet tested; this is the central research gap
Indirect: binary Fe ₂ O ₃ /TiO ₂ DSSC	(Da Cunha et al., 2026)	Fe ₂ O ₃ -modified photoanode	TiO ₂	Shows the effect of Fe ₂ O ₃ loading on photovoltaic performance
Indirect: binary graphene/TiO ₂ DSSC	(Anish Madhavan et al., 2012; Dang et al., 2021; Singh et al., 2022; Tang et al., 2018; Yang et al., 2010) (Makal & Das, 2021; Peiris et al., 2021)	rGO- or graphene-modified TiO ₂ photoanodes		Shows the effect of graphene content on charge transport and efficiency
Indirect: ternary, non-DSSC	(Botsa, 2025)	rGO-assisted composite used for photocatalysis	TiO ₂ –Fe ₂ O ₃ used for	Shows feasibility of combining the three phases; no photovoltaic data

TiO₂ remains the most widely used photoanode material due to its chemical stability, electronic properties, and high dye adsorption capability. In binary systems, graphene and rGO enhance electron transport by providing conductive pathways, while Fe₂O₃ extends the optical response of TiO₂ into the visible region and modifies interfacial charge transfer. Both modifications can enhance photovoltaic performance, provided composition, morphology, and loading are appropriately selected. The optimal loading is non-monotonic: moderate amounts of Fe₂O₃ or graphene are beneficial, while excessive loading introduces recombination centers, reduces optical transparency, or degrades morphology. However, the extent of improvement is strongly dependent on composition, processing

conditions, dye, electrolyte, photoanode thickness, and device architecture, making direct comparison across studies difficult.

The Fe₂O₃–graphene/TiO₂ ternary architecture is scientifically motivated by the complementary roles of its components: Fe₂O₃ extends visible-light absorption, graphene accelerates electron transport, and TiO₂ provides the semiconductor framework and dye-adsorbing surface. Limited photocatalytic evidence (Botsa, 2025) establishes the chemical feasibility of combining all three phases with functional benefit. However, the photovoltaic superiority of this ternary architecture over optimized binary systems has not been demonstrated.

Direct photovoltaic evidence from fully integrated Fe₂O₃-graphene/TiO₂ DSSC photoanodes remains scarce. No study identified in this review reported a complete set of photovoltaic parameters (J_{sc}, V_{oc}, FF, PCE) for a fully integrated ternary DSSC photoanode. Co-optimization of Fe₂O₃ loading, graphene content, TiO₂ morphology, and interfacial architecture remains unexplored. Long-term operational stability, reproducibility, and scalable fabrication of ternary photoanodes have not been systematically assessed.

A second gap concerns systematically optimizing the ternary composition. It is not only Fe₂O₃ and graphene derived materials that can enhance the performance of DSSC with the proper concentration, but too high or too low concentration of any of these can have adverse effects on morphology, dye adsorption, optical properties, charge transport or charge recombination of the DSSC. The optimal balance between Fe₂O₃ content and graphene concentration and TiO₂ loading has yet to be precisely tailored, and systematic studies that change Fe₂O₃ and the concentration of the graphene while maintaining constant fabrication and testing conditions, are required to make clear composition performance relations.

Another area of interest is the lack of understanding of the charge transfer mechanisms in the Fe₂O₃/graphene/TiO₂ interfaces. The enhanced photoelectrocatalytic performance of modified TiO₂ photoanodes has been attributed to several factors, such as reduced recombination and increased charge transport, but the pathways of electron transfer, energy levels at the interfaces and recombination processes in a complete ternary structure of a film remain not fully understood. The ability to obtain a clear picture will likely depend on using multiple complementary techniques such as XPS, Raman spectroscopy, photoluminescence, EIS, transient photocurrent determination etc. to establish the structure property performance relationships.

Literature also has a problem of directly comparing across studies. Various combinations of dyes, electrolytes, photoanode thickness, TiO₂ morphology, method of fabrication, area of measurement, and conditions of measurement are used in different groups, and some papers do not report all the important parameters such as J_{sc}, V_{oc}, fill factor or PCE. These differences make it difficult to compare quantitative data, and suggest the need for greater uniformity in reporting and testing procedures for ternary photoanodes.

Lastly, most of the work reported thus far remains at the laboratory scale, with little information on long term operational stability, environmental durability, reproducibility, and scalable fabrication. Future research must identify solutions to these practical challenges in addition to improving the raw PV efficiency of Fe₂O₃-graphene/TiO₂ photoanodes if they are to be taken out of the lab. Finally, developing a truly well-optimized

ternary photoanode requires thinking about composition, morphology, interfacial chemistry, charge transfer kinetics, PV performance, and long-term stability all at once.

Current Challenges

Despite the potential of Fe₂O₃-graphene/TiO₂ ternary nanocomposites, there are a number of challenges to overcome before it can be used in practice.

One of the largest challenges is to disperse graphene uniformly throughout the TiO₂ matrix. Van der Waals forces cause the sheets of graphene to agglomerate, decreasing the effective surface area and electron transportation. The control of distribution and loading of Fe₂O₃ nanoparticles is also challenging: excessive Fe₂O₃ promotes the occurrence of defect sites, which are recombination centers and affect the efficiency, and insufficient Fe₂O₃ does not significantly enhance the visible light absorption.

Another challenge posed by weak bonding at the interface is that the interfacial contact between TiO₂ and graphene and Fe₂O₃ is not strong enough, which consequently increases the resistance to charge transfer and diminishes the synergism of the ternary composite that is the main advantage of this composite material.

There's even the issue of scalability. Even though many synthesis methods work very well in the laboratory, such as hydrothermal and solvothermal methods, they are difficult to use on an industrial scale due to high energy consumption, long reaction times and high cost of the equipment. Another challenge is device stability as time goes on, dye molecules undergo degradation, solvent evaporation, electrolyte leakage, and overall photoanode degradation while operating in the light, all of which compromise long term efficiency, making the devices less competitive and less likely to be commercialized.

Future Perspectives

Future research on Fe₂O₃-graphene/TiO₂ ternary photoanodes must go beyond the demonstration of the individual performance improvement, and the systematic optimization of composition, interfaces, morphology and device architecture. It is important to establish clear, quantitative relationships between Fe₂O₃ loading, graphene content, TiO₂ morphology, interfacial bonding, and the PV parameters. Controlled studies systematically changing Fe₂O₃ and graphene concentrations under identical fabrication and testing conditions would provide much more compelling evidence of synergistic effects between Fe₂O₃ and graphene, and could provide fair comparisons between ternary and binary photoanodes.

The engineering of the interface is also worthy of special mention. Complementary structural, spectroscopic and electrochemical studies of the energy band alignment and electron transfer pathways between the TiO₂, Fe₂O₃ and

graphene are needed for future studies. Complementary use of XPS, Raman spectroscopy, HRTEM, PL, EIS, transient photocurrent and related measurements could distinguish true improvement in charge separation from changes that are more a matter of morphology or surface area, leading to a more robust understanding of the mechanism to guide further optimization of the ternary photoanodes.

The synthesis techniques should be increasingly reproducible, less energy consuming, and more scalable. Laboratory methods like hydrothermal, solvothermal and sol–gel are still viable, but future work should be aimed at developing other scalable methods that are capable of evenly distributing Fe₂O₃ and maintaining a high interfacial contact. Control over particle size, dispersion of graphene, film thickness, porosity and heterojunction architecture will be crucial to make the lab findings a reality in working DSSC devices.

Standardized photovoltaic testing and long-term stability should be given more emphasis in future studies. Reporting of J_{sc}, Voc, fill factor, PCE, incident photon to current conversion efficiency, and parameters and testing conditions consistently would make comparing results between different studies much easier; stability should be measured under prolonged illumination, thermal cycling, humidity exposure and operating cycles repeated, rather than just initial efficiency measurements. Such would clarify if the benefits of ternary photoanodes do indeed last over time.

Lastly, synthesis parameter-to-photovoltaic performance prediction and statistical optimization/machine learning-assisted materials design may be helpful for finding optimum Fe₂O₃/graphene compositions and understanding the relationship between the synthesis parameters and photovoltaic properties, if based on experimentally proven data. Systematic experiments, high level characterization and computational optimization appear to be the most promising approaches for achieving more efficient, reproducible, stable and scalable Fe₂O₃-graphene/TiO₂ photoanodes.

CONCLUSION

DSSCs remain an attractive third-generation photovoltaic technology owing to low fabrication cost, simple architecture, and operation under diffuse and low-intensity light. However, the photovoltaic efficiency, charge recombination, and stability of conventional TiO₂-based photoanodes remain significant challenges. This review has examined recent progress in Fe₂O₃-, graphene-, and TiO₂-based photoanodes for DSSCs, with emphasis on literature published from 2020 to 2026.

In binary systems, graphene and rGO improve electron transport, and Fe₂O₃ extends the visible-light response of TiO₂. Both can raise photovoltaic performance at moderate loading, while excessive loading promotes recombination or degrades morphology.

The complementary roles of the three components, together with limited photocatalytic evidence for a ternary composite make the ternary architecture a plausible route to better light harvesting, electron transport and charge separation.

No study identified in this review reports a complete set of photovoltaic parameters (J_{sc}, Voc, FF, PCE) for a fully integrated ternary DSSC photoanode. Its superiority over optimized binary systems, and its long-term stability and scalability, have not been shown.

The most important conclusion of this review is that the ternary Fe₂O₃-graphene/TiO₂ photoanode should be regarded as a scientifically motivated hypothesis rather than an established superior architecture. The principal research priority is to conduct systematic, standardized, and directly comparable studies of fully integrated ternary photoanodes under DSSC operating conditions, with complete reporting of photovoltaic parameters, comprehensive characterization of composition–interface–transport relationships, and rigorous assessment of long-term stability.

Such studies are required to determine whether the complementary mechanisms of the three components can be realized in practice to produce reproducible improvements in DSSC efficiency and durability.

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