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Review article



Towards high-performance dye-sensitized solar cells by utilizing reduced graphene oxide-based composites as potential alternatives to conventional electrodes: A review

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ABSTRACT

Dye-sensitized solar cells (DSSCs) have recently emerged as one of the most promising new-generation photovoltaic devices due to their facile fabrication protocols, capacity to operate under diffuse light, and low-impact on the environment. However, their low power conversion efficiency (~15.2%) hinders practical applications. This is primarily owing to ineffective dyes, significant recombination at solid/liquid interfaces, and limitations of TiO₂, the conventional photoanode material, especially poor light harvesting and electron transport. Moreover, Pt, the traditional counter electrode material, is costly and unstable due to its scarcity and low corrosion resistance to I₃⁻, respectively. This increases the device cost and shortens its lifespan. Inspired by this, current research interests have shifted their focus from traditional materials to low-cost alternatives, including metal oxides, metal chalcogenides and perovskites, which offer competitive photovoltaic performance. Nonetheless, these alternative materials exhibit relatively low electrical conductivity, which compromises device performance. Thus, to improve device efficiency and sustainability, these materials have recently been coupled with highly conductive and stable carbon nanomaterials, particularly graphene-based materials. Among them, reduced graphene oxide (rGO) has been more appealing due to its compatibility with low-cost solution processing. Therefore, this review highlights the recent advances in DSSC efficiency and sustainability made over the last five-years (2020–2024) by developing TiO₂-free photoanodes and Pt-free counter electrodes, in particular, by introducing rGO into metal oxides, metal chalcogenides and perovskites. Challenges and future directions for fabricating TiO₂- and Pt-free DSSCs are discussed to close the gap between emerging nanomaterials and their traditional counterparts, thereby setting the stage for commercialization.

1. Introduction

Almost 80% of the daily global energy consumption is generated from fossil fuels, such as coal, natural gas and oil [1–6]. However, these traditional energy sources will soon fail to meet the increasing energy demand due to their non-renewable nature, which is causing their rapid depletion. Also, the continuous usage of fossil fuels is becoming a serious

threat to the well-being of humans and the environment since fossil fuels release greenhouse gases that cause undesirable effects, such as pollution, global warming, acid rain and climate change [7–12]. Consequently, renewable energy sources, such as geothermal [13,14], biomass [15,16], wave [17,18], wind [19,20], solar [21,22] and hydropower [23,24], have emerged as potential solutions to resolve the global energy crisis. Among these, solar energy has gained intensive research

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attention owing to its low-cost due to the natural abundance of free sunlight, and low impact on the environment due to the absence of carbon emissions.

Meanwhile, dye-sensitized solar cells (DSSCs), one of the new-generation photovoltaic devices, have recently emerged as a promising renewable energy technology for converting solar energy into electricity due to their simple fabrication protocols, diverse designs and orientation flexibility, low-costs, flexibility and capability to function even under diffuse light [25–30]. DSSCs were initially conceptualized in the late 1980s [31], and they made a considerable breakthrough in 1991 when Grätzel and O'Regan developed a high-performing DSSC with a power conversion efficiency (PCE) of ~8% using a mesoporous TiO₂ photoanode, a Ru(II) pyridyl complex dye, and an I⁻/I₃⁻ redox electrolyte [32]. This device marked a substantial shift from traditional p-n junction solar cells by utilizing photoinduced electron injection into TiO₂ photoanodes of a dye-sensitized system. Subsequent research efforts have significantly increased device efficiency, stability and scalability through innovations in dyes, electrodes, and electrolytes [33–35]. In particular, the development of Ru-based dyes, D-π-A structured organic dyes, and porphyrin dyes has been central to improving visible light absorption and exciton dissociation [36]. Advances in photoanodes, especially those made from TiO₂ nanostructures, have been key to enhancing visible light harvesting and electron transport [37]. The development of high-performance counter electrodes, particularly those using Pt or carbon nanomaterials, has increased charge collection efficiency [38]. Innovations in liquid and quasi-solid-state electrolytes have enhanced the overall stability and ionic conductivity [39]. As a result, the PCE of the current state-of-the-art DSSCs based on two newly developed co-sensitizers has reached up to ~15.2% [40]. This, in turn, has expanded the potential applications of DSSCs to include indoor energy harvesting [41]. Despite these advancements, challenges remain in achieving competitive efficiency and long-term stability, prompting ongoing research and innovation in this field.

One such pressing issue arises from setbacks in one of the key DSSC components, the photoanode, which suffers from shortcomings of TiO₂ as the traditional semiconducting layer material. For example, TiO₂ displays poor light absorption in the visible region [42,43], which impairs electron-hole pair generation. TiO₂ also exhibits poor electron transport [43,44], which causes ineffective exciton dissociation with high recombination. This ultimately shortens the electron lifetime, resulting in state-of-the-art DSSCs with low PCEs that are ~58% of their first-generation counterparts (commercially available crystalline silicon solar cells) [45]. Additional major challenges are linked to Pt, the conventional counter electrode material, which is expensive due to its scarcity, and has poor stability in the electrolyte medium due to its low resistance to corrosion from I₃⁻ [46–50]. This increases the cost of DSSCs and shortens their lifetime.

Being motivated by this, significant research efforts have been recently directed towards developing potential alternatives to the traditional TiO₂ and Pt electrode materials, including semiconducting metal oxides [51,52], metal chalcogenides [53,54] and perovskites [55, 56], with competitive photovoltaic performance, excellent stability and low-costs. However, on their own, these materials exhibit relatively low electrical conductivity [57,58], which lowers device performance. This, in turn, necessitates the integration of these alternative materials with highly conductive materials to facilitate synergistic interactions that help in overcoming the limitations of individual materials, while also complementing their merits to improve device performance.

One such promising class of conductive materials is the emerging carbon nanomaterials family [59–62], specifically graphene and its derivatives, including graphene oxide (GO) and reduced GO (rGO), which show facile synthesis procedures and remarkable physicochemical properties [63–67]. This benefits from the merits of graphene, including its high specific surface area, wide visible light absorption spectrum and high electrical conductivity [68,69]. These merits promote effective dye adsorption, enhanced photon harvesting and efficient

electron transport with minimum recombination in DSSC photoanodes. Furthermore, the low charge transfer resistance and high electrocatalytic activity of graphene-based counter electrode nanomaterials are beneficial for enhancing the transfer of electrons from an external circuit to the electrolyte for catalyzing I₃⁻ reduction [70,71]. Most importantly, the high mechanical, thermal and chemical stabilities of graphene-based materials prolong the device lifespan [72,73]. On the other hand, their inexpensive nature owing to the inherent abundance of carbon lowers the device cost, and their non-toxicity allows for the fabrication of devices that are safe to use.

However, despite the promising potential of graphene-based composites with metal oxides, metal chalcogenides and perovskites to address the issues of traditional electrode materials in DSSCs, to the best of our knowledge, their practical application has been relatively less explored. Hence, this review seeks to advance the fabrication of efficient, durable and low-cost DSSCs by highlighting the recent breakthroughs in TiO₂-free photoanodes and Pt-free counter electrodes achieved during the last five-years (2020–2024), by employing the aforementioned graphene-based composite materials as photoanodes and counter electrodes. Merits, disadvantages and future research directions for developing TiO₂-free photoanodes and Pt-free counter electrodes are also discussed to provide a link-bridge for practical applications.

2. Graphene-based materials

Graphene, a two-dimensional semiconducting material, is made up of a single layer of *sp*²-hybridized carbon atoms with a hexagonal lattice structure (Fig. 1(a)). Graphene has been commonly prepared using top-down approaches, e.g., exfoliation [74–81], where stacked graphite layers are separated into few layers of graphene sheets, and bottom-up approaches, e.g., chemical vapour deposition (CVD) [82–91], in which graphene is synthesized at high temperatures from either elemental carbon or carbon radicals. The application of graphene in photovoltaic devices has been made possible by its interesting properties, such as excellent stability, large specific surface area, tunable zero band gap, broad and intense absorption spectrum, high visible region transparency, and high electrical conductivity [92–98]. However, like other carbon-based materials, such as carbon nanotubes, nanospheres, nanofibers and nanofibers, graphene has limitations emanating from its hydrophobicity, insolubility and poor dispersion in many organic solvents due to its chemical inertness [99–101]. This makes graphene incompatible with low-cost solution processing during DSSC device fabrication. To overcome these drawbacks, the oxidation-reduction method has been recently used to prepare oxygen-functionalized derivatives of graphene, i.e., GO and rGO (Fig. 1(b-c)), with better solubility and dispersion than graphene.

The abundance of oxygen functional groups enhances the chemical reactivity of GO and renders GO with superior hydrophilicity and good dispersibility in many solvents, especially polar solvents, facilitating the compatibility of GO to low-cost solution processing [101,102]. Nonetheless, the oxygen-containing functional groups disrupt the conductive properties of GO, making it an insulator [103], which limits its application in DSSCs. Hence, GO is commonly reduced by removing some of its oxygen functional groups to prepare rGO. This restores electron delocalization and increases electrical conductivity. The remaining oxygen functional groups in rGO play a critical role in facilitating strong synergistic interactions with other active materials [104,105]. This not only enhances the stability of the resulting composite material, but also improves its optoelectronic properties. However, during reduction, electron delocalization is partially restored, which compromises the optoelectronic properties of rGO. Therefore, to optimize the optoelectronic properties of rGO and make them competitive to those of graphene in DSSC applications, rGO has been recently doped with heteroatoms, such as B and N [106], as well as being incorporated into novel semiconducting materials, including metal oxides [107], metal

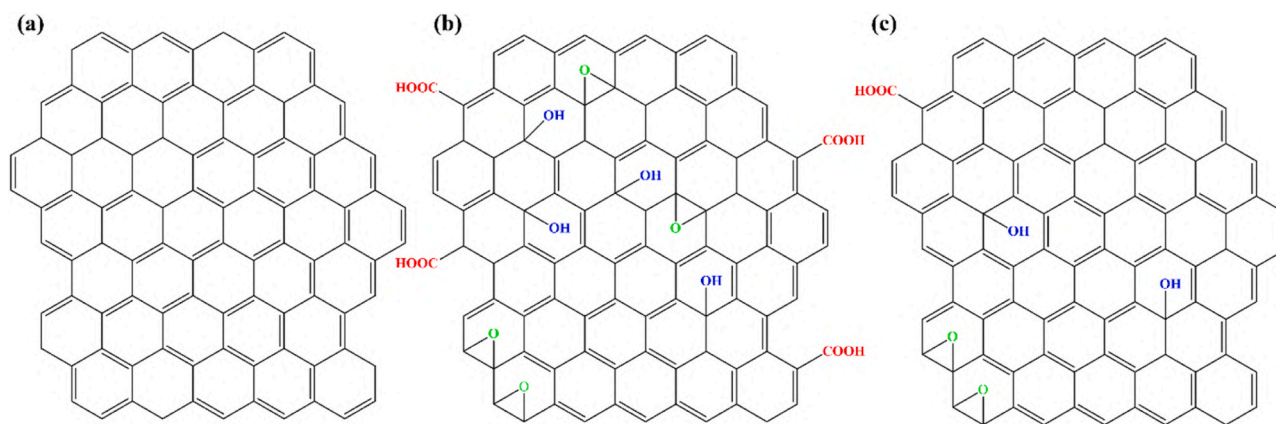


Fig. 1. Molecular structure of (a) graphene, (b) GO and (c) rGO.

chalcogenides [108] and perovskites [55], to form nanocomposites, as discussed in the following sections.

3. Photoanode

A dye-loaded semiconducting metal oxide material is deposited on a transparent conducting oxide material to prepare a DSSC photoanode responsible for photon-to-electricity conversion [109,110]. Thus, an efficient photoanode material should be highly transparent to allow for the entrance of more light into the cell. It must also be mesoporous with a high specific surface area to provide numerous active sites that effectively adsorb dye molecules for efficient light harvesting. A highly conductive photoanode also promotes rapid electron transport with minimum recombination. A photoanode material should also be constituted by relatively large particles to prevent unabsorbed light from being transmitted through the photoanode by scattering it back to the dye-coated semiconductor to facilitate effective photon harvesting. Furthermore, the photoanode should provide proper alignment of the conduction band with the lowest unoccupied molecular orbital (LUMO), i.e., it should be well below the dye LUMO to facilitate efficient electron transfer [111,112]. A good photoanode should also exhibit high stability in the electrolyte system to prolong the device lifetime.

An assortment of wide band gap semiconducting metal oxides, such as TiO_2 [113,114], Nb_2O_5 [115,116], SnO_2 [117,118] and ZnO [119, 120], have been employed over the years to fabricate DSSC photoanodes. Among them, TiO_2 has been widely recognized as the conventional semiconducting layer material owing to its ease of availability and non-toxicity, which make it inexpensive [121–124], as well as its excellent photochemical stability [125–127], which increases device lifetime. Additionally, the mesoporous nature of TiO_2 provides the photoanode with a large surface area beneficial for enhancing dye adsorption.

Nevertheless, TiO_2 exhibits a relatively low optical transmittance in the visible region, which limits the passage of more light into the cell. TiO_2 also has a wide band gap (~ 3.2 eV), which permits the harvesting of ultraviolet (UV) light only, resulting in poor visible light absorption [128–130]. The TiO_2 wide band gap also provides a large energy barrier at the dye/semiconductor interface. This causes poor injection of electrons from the dye molecule LUMO to the TiO_2 conduction band, as well as high recombination of photogenerated electrons with oxidized dye molecules and I_3^- in the electrolyte. Thus, TiO_2 has been commonly integrated with highly transparent materials to increase its transmittance in the visible region, and medium or narrow band gap materials to reduce its band gap to extend the absorption spectrum from the UV to the visible region [131]. This enhances photon harvesting and promotes exciton generation. Medium or narrow band gap materials also lower the energy barrier at the dye/ TiO_2 interface, which promotes the effective dissociation of electron-hole pairs and the efficient

injection of photogenerated electrons from the LUMO of dye molecules to the TiO_2 conduction band with minimum recombination.

The small-sized TiO_2 nanoparticles show many defects and grain boundaries. These allow for the transmission of unabsorbed light through the photoanode due to their inability to effectively scatter unabsorbed light back to the photoanode, thereby causing poor photon harvesting. The numerous defects and grain boundaries also cause TiO_2 to have poor electron transfer properties with high recombination rates [132]. As a consequence, a light-scattering layer has been commonly prepared by introducing larger TiO_2 particles with dimensions comparable to the wavelength of visible light [133]. This prevents unabsorbed light from passing through the photoanode by reflecting it to the photoanode itself to enhance light harvesting for effective exciton generation to occur. TiO_2 has also been integrated with highly conductive materials, which provide additional electron transport pathways beneficial for improving electron transfer with low recombination losses [134]. In addition, post-synthesis treatments of TiO_2 , e.g., with TiCl_4 solution [135], and thermal annealing [136], have also been employed to repair the surface defects, which, in turn, reduces the number of charge carrier scattering centres, resulting in rapid electron transport with minimum recombination.

The mesoporous TiO_2 film also permits direct contact between the electrolyte and bare sites of the transparent conducting electrode, resulting in recombination between I_3^- in the electrolyte and photo-generated electrons on the transparent conducting electrode [137]. This shortens the electron lifetime, leading to poor photovoltaic performance. As a result, a compact layer has been commonly deposited at the transparent conducting electrode/mesoporous TiO_2 interface to prevent direct contact between the electrolyte and the transparent conducting electrode to suppress recombination [138]. A compact layer also assists by smoothing out the transparent conducting electrode/ TiO_2 interface, which reduces issues with short-circuits and leakage current; hence, increasing device performance.

Despite the aforementioned efforts to modify the photovoltaic performance of TiO_2 , the PCE of state-of-the-art TiO_2 -based DSSCs ($\sim 15.2\%$) [40] remains lower than that of commercialized first-generation (crystalline silicon) solar cells ($>26\%$) [45]. As a result, recent research interests have shifted from TiO_2 to concentrate on emerging low-cost TiO_2 -free semiconducting layer materials, such as metal oxides [139–141], metal chalcogenides [142,143] and perovskites [144–146], with competitive photovoltaic performance and stability. However, in their pristine form, these alternative materials tend to aggregate, resulting in small surface areas with poor dye adsorption, ineffective light harvesting and low electrical conductivity. These semiconducting materials also have drawbacks due to their wide band gap. On the one hand, wide band gap causes poor visible light absorption by permitting the absorption of UV light only. On the other hand, wide band gap provides a large energy barrier that inhibits the effective

injection of photogenerated electrons from dye molecules to the semiconducting material. This, in addition to the low charge transfer rate of these semiconducting materials, causes poor exciton dissociation and high recombination of electrons with I_3^- in the electrolyte and oxidized dye molecules, which shortens the electron lifespan, resulting in poor device performance.

Inspired by this, these semiconducting materials have recently been coupled with highly conductive carbon nanomaterials, particularly rGO, with a large specific surface area [147] to supply more active sites for effective dye loading to improve visible light absorption and electron-hole pair generation. This also takes advantage of the residual oxygen functionalized groups in rGO, which enable it to strongly bind with active materials to enhance charge transfer and device stability [104,105]. The introduction of rGO, a narrow band gap material, also helps to lower the band gap of the semiconducting material. This, in turn, widens the absorption spectrum to the visible region to improve light harvesting and electron-hole pair generation. Simultaneously, the energy barrier is lowered to enhance exciton dissociation and electron transfer with low recombination losses.

Similar to the above-mentioned pristine semiconducting materials, pristine rGO nanosheets tend to aggregate and restack [97,148], which reduces the photoanode surface area, resulting in poor dye loading and low photon absorption. This also compromises electron transport, giving rise to high recombination rates, and hence low short-circuit current density (J_{sc}) and PCE. Interestingly, the preparation of rGO-based composites with the aforementioned semiconductor materials helps to prevent the aggregation of the individual constituents. Therefore, it minimizes the loss of specific surface area, enhances dye loading and visible light absorption, and reduces interfacial charge transfer resistance. This not only helps to overcome the setbacks of the individual constituents, but also those of TiO_2 , the traditional photoanode, as discussed in Section 4.

4. Reduced graphene oxide-based TiO_2 -free photoanodes

The recent applications of rGO-based composites with semiconducting metal oxides, metal chalcogenides and perovskites, as promising alternatives to TiO_2 photoanodes in DSSCs, have been discussed in Sections 4.1–4.3 and summarized in Tables 1–3, respectively.

Table 1

Photovoltaic parameters of DSSCs using metal oxide and rGO/metal oxide nanocomposite photoanodes. V_{oc} and FF represent the open-circuit voltage and the fill factor of the solar devices, respectively.

Semiconducting layer material	Dye	Redox couple	V_{oc} (V)	J_{sc} ($mA\ cm^{-2}$)	FF	PCE (%)	Ref.
CuO	N719	Γ/I_3^-	0.71	3.63	0.67	1.76	[149]
rGO/CuO			0.72	4.62	0.78	2.65	
CdO			0.72	4.86	0.72	2.64	
rGO/CdO	N719	Γ/I_3^-	0.74	6.48	0.68	3.53	[149]
SnO ₂			0.61	6.62	0.47	1.90	
rGO/SnO ₂			0.53	12.20	0.46	3.01	
CeO ₂	N719	Γ/I_3^-	0.50	6.90	0.50	1.74	[149]
rGO/CeO ₂			0.52	8.60	0.45	2.15	
Bi ₂ O ₃			0.53	6.00	0.21	0.42	
rGO/Bi ₂ O ₃	Eosin B	Γ/I_3^-	0.48	9.80	0.44	1.68	[150]
B-rGO/Bi ₂ O ₃			0.59	10.00	0.50	2.79	
N-rGO/Bi ₂ O ₃			0.55	9.20	0.47	1.97	
ZnO	N719	Γ/I_3^-	0.74	6.77	0.69	3.50	[149]
rGO/ZnO			0.73	8.52	0.70	4.44	
ZnO			0.43	0.20	0.38	0.33	
rGO/ZnO	N719	Γ/I_3^-	0.46	0.24	0.52	0.57	[151]
ZnO			0.58	1.18	0.66	0.45	
rGO/ZnO			0.54	1.60	0.56	0.50	
ZnO	N719	Γ/I_3^-	0.35	2.33	0.56	0.46	[153]
rGO/ZnO			0.39	4.65	0.59	1.07	
rGO/ZnO			0.20	2.68	0.29	0.16	
rGO/ZnO-Fe ₂ O ₃	N719	Γ/I_3^-	0.60	1.75	0.40	0.42	[154]
ZnO			0.58	6.40	0.51	1.90	
rGO/ZnO			0.73	8.15	0.60	3.58	
rGO/Sr-ZnO			0.70	18.40	0.61	7.90	[155]

4.1. Reduced graphene oxide/metal oxide nanocomposites

Recently, rGO has been introduced into metal oxides, such as CuO, CdO, SnO₂, CeO₂ [149], Bi₂O₃ [150], ZnO [149,151–153], ZnO-Fe₂O₃ nanocomposites [154] and Sr-doped ZnO (Sr-ZnO) [155]. Among other advantages, the rGO sheets provide better energy band alignment at the dye/photoanode interface, which facilitates the fast transfer of photo-generated electrons from the LUMO of dye molecules to the metal oxide conduction band with minimum recombination. This increases the electrical conductivity of the photoanode, e.g., as demonstrated by the significant increase in the slope of the current-voltage (I - V) curves of rGO-based composites (Fig. 2(a)), which ultimately increases the J_{sc} (Fig. 2(b)), and hence improves the DSSC performance [150]. For example, DSSCs based on rGO/metal oxide composite photoanodes have recently displayed comparable photovoltaic performance to their traditional TiO_2 -based counterparts, e.g., by reaching up to ~87% of the PCE of TiO_2 reference devices [149]. Also, the rGO/metal oxide-based DSSCs have surpassed the PCE of pristine metal oxide devices, e.g., by ~564% [150] and ~133% [153], demonstrating the significant role played by rGO towards improving device performance. Thus, rGO/metal oxide composites can be used in future research as promising alternatives to not only the conventional TiO_2 photoanodes, but also to their pristine metal oxide counterparts.

4.2. Reduced graphene oxide/metal chalcogenide nanocomposites

Metal chalcogenides, such as CuS [156], MoS₂ [157] and WS₂ [158], have also been integrated with rGO, and used as potential alternatives to the traditional TiO_2 photoanodes in DSSCs. Among other merits, the mesoporous nature of the resulting materials, revealed by the type IV N_2 adsorption-desorption isotherms with a characteristic H3 hysteresis loop (Fig. 3(a)) [157], provides a large photoanode surface area, which allows for optimum distribution of dye molecules on the semiconducting layer with minimum agglomeration. This, in addition to the large specific surface area of rGO, improves dye loading and increases visible light absorption for effective photogeneration of electrons to occur. At the same time, a significant reduction in pore diameter upon the formation of the composites was revealed by the Barrett-Joyner-Halenda (BJH) pore size distribution curves (Fig. 3(b)) [157]. This helps to

Table 2

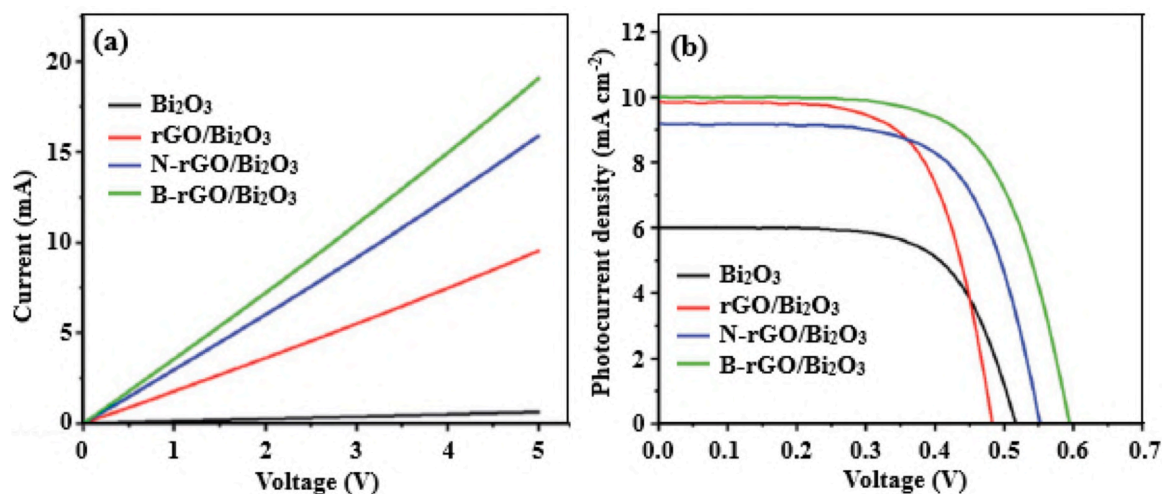
Photovoltaic parameters of DSSCs using metal chalcogenide and rGO/metal chalcogenide nanocomposite photoanodes.

Semiconducting layer material	Dye	Redox couple	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref.
CuS			0.64	11.10	0.56	4.27	
rGO	N719	Γ/I_3^-	0.48	9.20	0.48	2.08	[156]
rGO/CuS			0.71	16.00	0.70	7.81	
MoS ₂			0.67	9.32	0.52	3.36	
rGO	N719	Γ/I_3^-	0.58	6.94	0.46	1.23	[157]
rGO/MoS ₂			0.82	15.82	0.71	8.92	
WS ₂			0.68	11.80	0.62	4.20	
rGO	N719	Γ/I_3^-	0.59	9.20	0.52	2.10	[158]
rGO/WS ₂			0.79	18.60	0.66	9.60	

Table 3

Photovoltaic parameters of DSSCs using perovskite and rGO/perovskite nanocomposite photoanodes.

Semiconducting layer material	Dye	Redox couple	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref.
ZnTiO ₃			0.66	1.90	0.34	0.43	
rGO/ZnTiO ₃	N719	Γ/I_3^-	0.65	4.27	0.40	1.11	[159]
SrTiO ₃			0.76	6.98	0.49	2.59	
rGO/SrTiO ₃	N719	Γ/I_3^-	0.77	11.16	0.63	5.42	[160]
BaTiO ₃			0.73	7.50	0.56	3.07	
rGO/BaTiO ₃	N719	Γ/I_3^-	0.73	15.02	0.54	5.92	[161]
BaSnO ₃			0.67	11.01	0.52	3.82	
rGO/BaSnO ₃	N719	Γ/I_3^-	0.70	13.96	0.57	5.59	[162]
rGO			0.62	8.17	0.51	3.98	
rGO/SSFC	Eosin B	Γ/I_3^-	0.74	13.15	0.59	7.01	[163]

**Fig. 2.** (a) Current-voltage characteristics, and (b) photocurrent density-voltage curves of pristine Bi₂O₃ and rGO/Bi₂O₃-based composites. Adapted under a Creative Commons license [150], Copyright (2022), open access.

suppress the recombination of electrons on the transparent electrode and I_3^- in the electrolyte by reducing the amount of electrolyte that penetrates through the photoanode to reach the transparent electrode. Low charge carrier recombination favourably results in high electron density, which increases the J_{sc} , and causes a shift in the Fermi level, which increases the open-circuit voltage (V_{oc}), thereby increasing the PCE. For example, the rGO/WS₂ composite photoanode-based DSSCs displayed an optimum PCE of $\sim 10\%$, which surpassed that of pristine WS₂- and rGO-based devices by ~ 129 and 357% , respectively [158], highlighting the superiority of rGO/metal chalcogenide composites.

The excellent chemical, mechanical and thermal stability of rGO is also beneficial for complementing the high stability of metal chalcogenides. This helps to increase the device lifetime, e.g., as demonstrated by the ability of rGO/CuS-based DSSCs to retain $\sim 95\%$ of the initial PCE after exposure to light illumination for 21 days [156]. This outperformed the devices based on pristine rGO and CuS photoanodes, which maintained ~ 85 and 88% of their original PCEs, respectively,

under the same conditions. In a similar study, rGO/MoS₂-based DSSCs managed to maintain above 95% of the original PCE after a relatively longer period of 60 days (Fig. 4) [157]. Thus, the introduction of rGO into metal chalcogenides to form rGO/metal chalcogenide composites not only increases the device efficiency, but also enhances the device stability, both of which are critical for practical and commercial applications.

4.3. Reduced graphene oxide/perovskite nanocomposites

Perovskite metal oxide semiconductor materials, such as ZnTiO₃ [159], SrTiO₃ [160], BaTiO₃ [161], BaSnO₃ [162] and Sr_{0.7}Sm_{0.3}Fe_{0.6}Co_{0.4}O₃ (SSFC) [163], have also been recently employed in combination with rGO, as promising alternatives for TiO₂ photoanodes in DSSCs. In addition to other advantages, this helps to prevent the aggregation of pristine perovskite oxide nanoparticles (Fig. 5(a)) and the restacking of wrinkled rGO sheets (Fig. 5(b)) [163], which would otherwise reduce

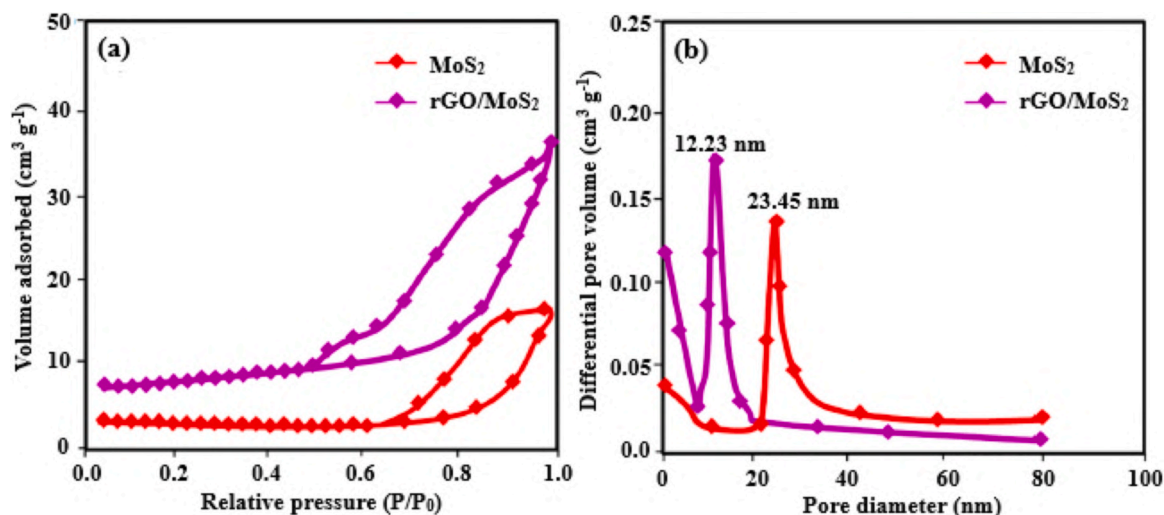


Fig. 3. (a) N_2 adsorption-desorption analysis, and (b) pore size distribution of pristine MoS_2 and the rGO/ MoS_2 composite. Adapted from [157], Copyright (2020), with permission from Elsevier.

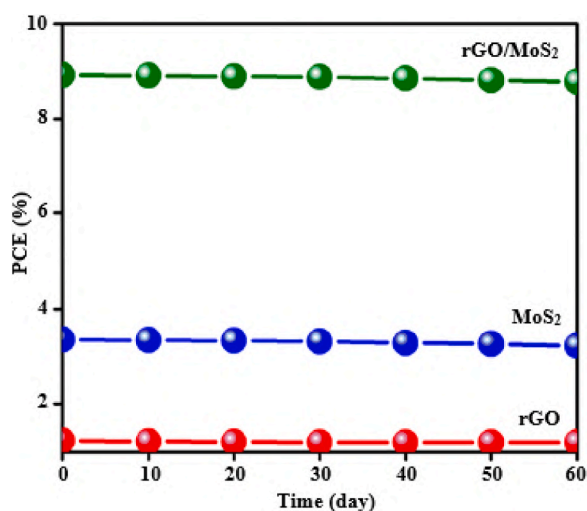


Fig. 4. Stability test of rGO-, MoS_2 - and rGO/ MoS_2 -based DSSCs. Adapted from [157], Copyright (2020), with permission from Elsevier.

the specific surface area of the photoanode, compromise dye loading and impede electron transport. As a result, the prepared nanocomposites were made up of a homogeneous dispersion of perovskite oxide nanoparticles on the rGO nanosheets (Fig. 5(c)) [163], which allowed for the provision of numerous active sites for not only improving the adsorption of dye molecules, but also for enhancing electron transport on the rGO/perovskite oxide nanocomposite surface.

When compared to pristine perovskite oxides, the superior dye-loading capacity of rGO/perovskite oxides is demonstrated in Fig. 6(a) by the higher absorbance of N719 dye molecules desorbed from the surface of rGO/ $BaTiO_3$ composites [161]. This indicates that the rGO/ $BaTiO_3$ composites initially adsorb more dye than pristine $BaTiO_3$ before desorption. Effective dye loading enhances light harvesting, which, in turn, improves exciton generation. This, in addition to the conductive nature of rGO, ensures effective exciton dissociation with minimum recombination, as revealed by the decrease in photoluminescence (PL) intensity (Fig. 6(b)) [161], thereby improving device performance. For example, DSSCs based on rGO/perovskite oxide composite photoanodes have managed to exceed the PCE of the pristine rGO, e.g., by $\sim 71\%$ [163], and pristine perovskite oxides, e.g., by $\sim 109\%$ [160]. Therefore, rGO has significant potential to improve the

performance of perovskite oxide photoanode materials in DSSCs.

5. Counter electrode

A conductive and catalytic material is deposited on a transparent conducting oxide material to prepare a DSSC counter electrode responsible for transferring electrons from an external circuit to the electrolyte to speed up the reduction of I_3^- to I^- for the subsequent regeneration of dye molecules [164–167]. Thus, a good counter electrode material should be highly conductive to enable the rapid transfer of electrons to the electrolyte, and highly electrocatalytic to speed up I_3^- reduction. An efficient counter electrode should also be highly reflective to prevent the loss of unabsorbed light transmitted through the photoanode by reflecting it to the sensitizer (dye molecules) to promote effective photon harvesting. Additionally, the counter electrode should be highly stable in the electrolyte system to prolong the device lifespan.

Meanwhile, Pt thin films deposited on a transparent conducting electrode have been widely used as the conventional counter electrode due to their high reflectance, low charge transfer resistance, high electrical conductivity and high electrocatalytic activity [168–171]. Nonetheless, Pt suffers from high-costs owing to its scarcity, and instability issues due to its poor corrosion resistance to I_3^- in the redox couple [172–181]. Although considerable research efforts have been made to improve device performance and stability, using approaches which include fabricating Pt-based nanocomposites with competitive electrical conductivity and electrocatalytic activity [182–184], the PCE and stability of Pt-based DSSCs have remained low. Therefore, the development of highly stable and low-cost Pt-free counter electrode materials with comparable electrical conductivity and electrocatalytic activity has recently emerged as one of the most promising strategies to overcome the aforementioned limitations.

Being motivated by this, numerous promising Pt-free counter electrode materials, such as metal oxides [185–187], metal chalcogenides [188–190] and perovskites [172,191], have been recently explored. This is primarily owing to their ability to facilitate electron hopping transport, which renders them with good electrocatalytic activity towards I_3^- reduction, in addition to their low-costs and excellent stability [192]. These alternative materials also have hierarchical structures with nanopores that allow for the exposure of more surface-active sites for electrocatalytic reactions, which speeds up the reduction of I_3^- . However, when compared to the conventional Pt counter electrode, the semiconducting nature of these alternative materials makes them have relatively low electrical conductivity and catalytic reduction

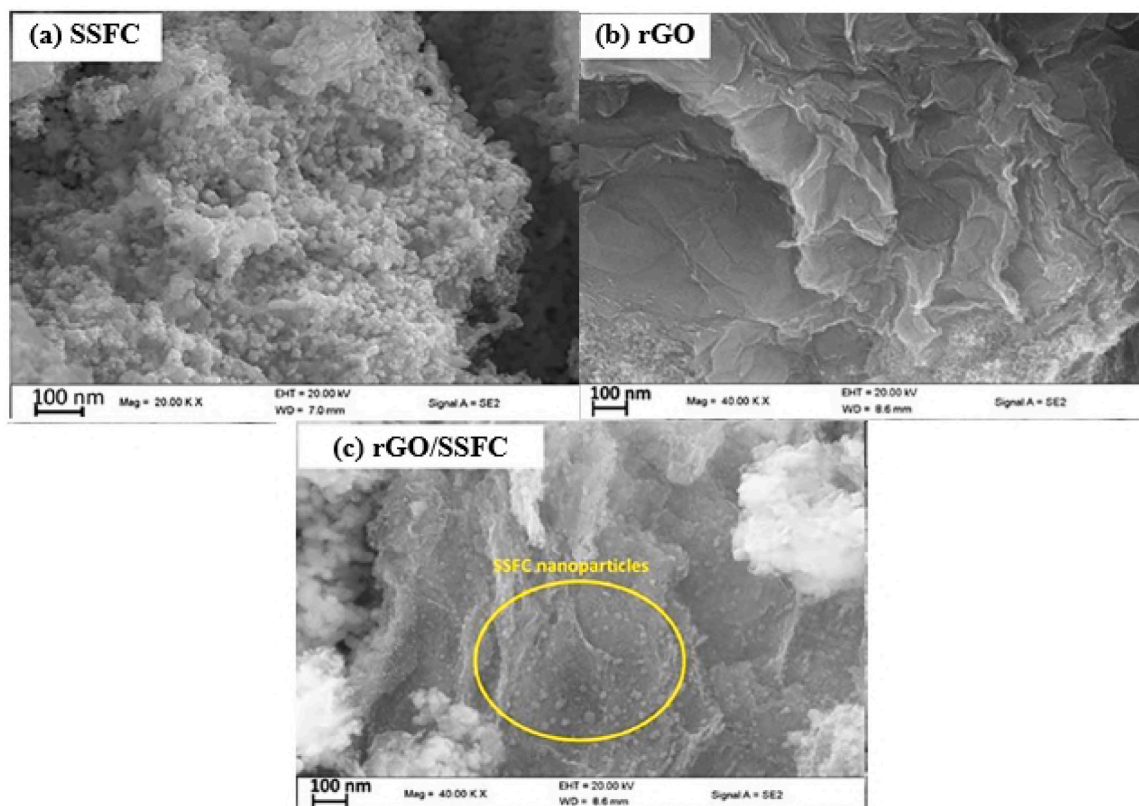


Fig. 5. Field-emission scanning electron micrographs of (a) SSFC, (b) rGO, and (c) rGO/SSFC. Adapted under a Creative Commons license [163], Copyright (2023), open access.

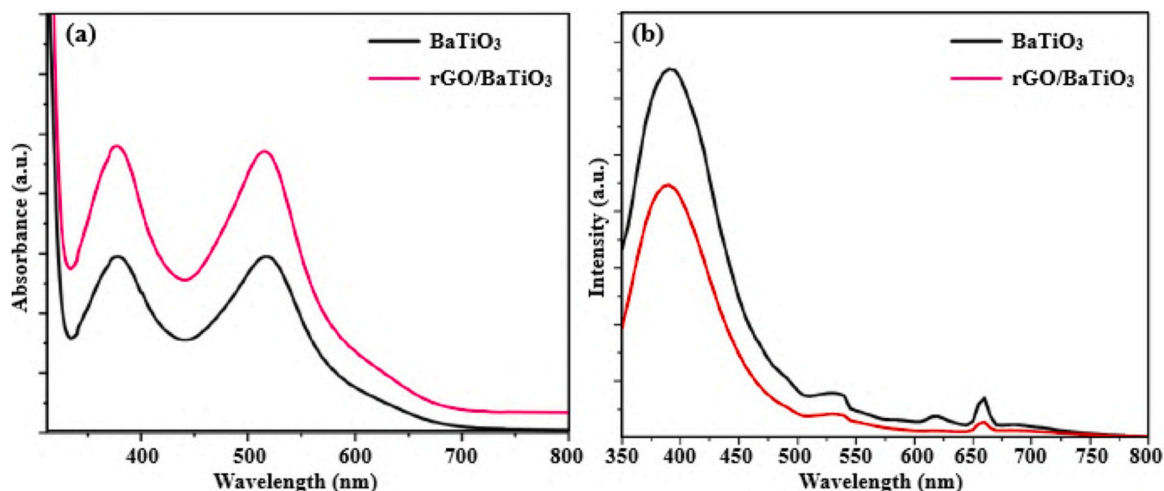


Fig. 6. (a) Absorption spectra of N719 dye molecules desorbed from the surface of pristine BaTiO₃ and rGO/BaTiO₃ composites, and (b) PL spectra of corresponding materials. Adapted from [161], Copyright (2024), with permission from Elsevier.

performance [174], both of which impair device performance. Thus, these alternative catalytic materials have been recently integrated with highly conductive and stable carbon nanomaterials, especially graphene-based materials, in particular, rGO, which is compatible with low-cost solution synthesis [193,194], to produce a significant enhancement in photovoltaic performance as discussed in Section 6.

6. Reduced graphene oxide-based Pt-free counter electrodes

The recent applications of rGO-based composites with semi-conducting metal oxides, metal chalcogenides and perovskites, as

potential replacements for Pt counter electrodes in DSSCs, have been discussed in Sections 6.1–6.3 and summarized in Tables 4–6, respectively.

6.1. Reduced graphene oxide/metal oxide nanocomposites

Recently, rGO has been introduced into various metal oxide-based counter electrodes, such as Co₃O₄ [195], Fe₃O₄ [192], α -Fe₂O₃ [196], MnO₂/NiO/CuO [197] and Cu₂ZnNiSe₄/WO₃ [198]. Among several advantages, this enables the large specific surface area and residual oxygen functionalized groups in rGO to support the uniform dispersion

Table 4

Photovoltaic parameters of DSSCs using metal oxide and rGO/metal oxide nanocomposite counter electrodes.

Counter electrode material	Dye	Redox couple	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref.
Co ₃ O ₄			0.42	8.30	0.19	0.87	
rGO	N719	Γ/I_3^-	0.71	16.02	0.26	3.05	[195]
rGO/Co ₃ O ₄			0.78	15.92	0.57	7.08	
rGO/Fe ₃ O ₄	N719	Γ/I_3^-	0.72	5.18	0.59	2.20	[192]
α -Fe ₂ O ₃			0.64	13.30	0.55	4.69	
rGO	N3	Γ/I_3^-	0.56	12.47	0.45	3.08	[196]
rGO/ α -Fe ₂ O ₃			0.65	15.43	0.61	6.12	
rGO/MnO ₂ /NiO/CuO	N719	Γ/I_3^-	0.75	13.46	0.76	7.67	[197]
rGO/Cu ₂ ZnNiSe ₄ /WO ₃	N719	Γ/I_3^-	0.88	24.70	0.56	12.16	[198]

Table 5

Photovoltaic parameters of DSSCs using metal chalcogenide and rGO/metal chalcogenide nanocomposite counter electrodes.

Counter electrode material	Dye	Redox couple	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref.
NiSe ₂			0.62	12.20	0.50	6.04	
rGO/NiSe ₂	N719	Γ/I_3^-	0.80	20.10	0.76	10.60	[199]
Ni _{0.85} Se			0.74	15.88	0.66	7.76	
rGO	N719	Γ/I_3^-	0.71	6.88	0.59	2.88	[200]
rGO/NiSe ₂			0.77	16.33	0.71	8.93	
Cu ₂ ZnNiSe ₄			0.68	17.50	0.33	3.88	
rGO/Cu ₂ ZnNiSe ₄	N719	Γ/I_3^-	0.86	21.21	0.48	8.75	[198]
rGO/Ni ₂ P ₅	N719	Γ/I_3^-	0.70	16.94	0.60	7.02	[201]
rGO/Ni ₁₂ P ₅			0.70	19.55	0.60	8.19	
rGO	N719	Γ/I_3^-	0.62	6.42	0.57	2.25	[202]
rGO/MoS ₂			0.72	6.91	0.64	3.19	
MoS ₂			0.72	13.60	0.51	5.00	
rGO	N719	Γ/I_3^-	0.73	13.90	0.52	5.20	[203]
rGO/MoS ₂			0.71	14.20	0.62	6.30	
MoS ₂			0.73	4.52	0.61	2.01	
rGO/MoS ₂	N719	Γ/I_3^-	0.74	7.80	0.68	3.92	[204]
rGO/N-GQD/MoS ₂			0.76	8.62	0.70	4.65	
rGO	N719	Γ/I_3^-	0.68	5.76	0.42	1.66	[205]
rGO/NiS ₂			0.67	9.02	0.52	3.16	
CoNi ₂ S ₄			0.61	13.14	0.72	5.78	
rGO	N719	Γ/I_3^-	0.55	10.68	0.58	3.44	[206]
rGO/CoNi ₂ S ₄			0.67	16.34	0.84	9.22	
CoNi ₂ S ₄			0.62	8.41	0.66	3.45	
rGO/CoNi ₂ S ₄	N719	Γ/I_3^-	0.88	21.96	0.85	10.21	[207]
FeNi ₂ S ₄			0.60	8.01	0.63	4.87	
rGO/FeNi ₂ S ₄	N719	Γ/I_3^-	0.87	20.04	0.84	9.98	[208]

of metal oxide nanoparticles possibly through chemical bonds. This results in the even distribution of catalytic metal oxide nanoparticles on the surface of conductive rGO sheets. For instance, the integration of spherically-shaped and agglomerated α -Fe₂O₃ nanoparticles of diameter 20–50 nm (Fig. 7(a)) with wrinkled and folded rGO sheets (Fig. 7(b)) led to the formation of evenly decorated α -Fe₂O₃ nanoparticles on the surface of the rGO sheets (Fig. 7(c)) [196]. This demonstrates the presence of a strong interaction between rGO sheets and metal oxide nanoparticles, which is beneficial for the efficient collection and transfer of photogenerated electrons. Moreover, the resulting rGO/ α -Fe₂O₃ composite film surface (Fig. 7(c)) exhibited a rough surface with numerous pores that are desirable for providing a large specific surface area with abundant oxidation sites for rapid I₃⁻ reduction. Therefore, in the rGO/metal oxide composite counter electrodes, the rGO sheets play a critical role by providing high-speed pathways for rapid electron transfer, while at the same time, the multilayer metal oxide

Table 6

Photovoltaic parameters of DSSCs using perovskite and rGO/perovskite nanocomposite counter electrodes.

Counter electrode material	Dye	Redox couple	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Ref.
rGO/La ₂ CrFeW ₆ /SO ₄ ²⁻			0.65	22.00	0.53	7.59	
rGO/La ₂ CrFeW ₆ /CO(NH ₂) ₂	N719	Γ/I_3^-	0.67	22.40	0.56	8.40	[191]
rGO/La ₂ CrFeW ₆ /CdSe			0.68	21.80	0.62	9.20	
rGO/La ₂ CrFeW ₆ /C ₆ H ₁₀ S ₃			0.68	26.10	0.59	10.40	
SSFC			0.73	12.44	0.40	4.06	
rGO	Eosin	Γ/I_3^-	0.64	10.38	0.49	3.29	[209]
rGO/SSFC	B		0.81	16.04	0.66	5.94	
N-rGO/SSFC			0.88	18.63	0.69	6.64	

nanoparticles on the rGO sheet surface provide numerous catalytically active sites for effective I₃⁻ reduction. Thus, the synergistic effects between the high electrocatalytic activity of metal oxides and the high electrical conductivity of rGO have the potential to improve the performance of Pt-free counter electrodes to compete with their Pt-based counterparts.

For example, DSSCs based on novel and low-cost rGO/metal oxide composite counter electrodes have recently exhibited comparable photovoltaic performance to those based on the traditional Pt counter electrode, e.g., reaching up to ~97% [195], ~93% [197], and ~88% [196] of the PCE of Pt-based reference devices. When compared to the rGO-based devices, the relatively high PCE of Pt reference devices can be ascribed to the superior electrical conductivity and electrocatalytic activity of Pt. The relatively low PCE of rGO-based devices can also be attributed to the poor reflectance of rGO-based counter electrodes. Poor reflectance prevents the reflection of unabsorbed incident light back to the photoanode. This contrasts with Pt, which has high reflectivity and facilitates the maximum utilization of unabsorbed incident light by reflecting it to the photoanode for electron-hole pair generation. Interestingly, the rGO/metal oxide-based devices outperformed their pristine metal oxide counterparts, e.g., by ~714% [195], and their pristine rGO-based DSSCs, e.g., by ~99% [196], demonstrating the critical role played by nanocompositing in improving device performance.

6.2. Reduced graphene oxide/metal chalcogenide nanocomposites

In recent years, rGO has been incorporated into metal chalcogenide counter electrodes, including selenides, e.g., NiSe₂ [199,200] and Cu₂ZnNiSe₄ [198]; phosphides, e.g., Ni₂P₅ and Ni₁₂P₅ [201]; sulfides, e.g., MoS₂ [202–204], NiS₂ [205], CoNi₂S₄ [206,207] and FeNi₂S₄ [208]. The successful formation of rGO/metal chalcogenide composites was confirmed by the appearance of characteristic diffraction peaks of both rGO and metal chalcogenides, e.g., NiS₂, in the XRD pattern of the composite (Fig. 8(a)) [205]. The presence of rGO in the composites was also confirmed by the appearance of D- and G-bands on the Raman spectra of the composites, e.g., rGO/NiS₂ (Fig. 8(b)). The D-band is associated with the presence of defects or disordered layers, while the G-band is ascribed to the presence of an ordered graphitic sp² carbon matrix. While the difference in the I_D/I_G ratio between the composite (1.07) and pristine rGO (1.04) may seem small and could fall within the error margin, it suggests the introduction of structural defects that enhance coupling between the conductive rGO sheets and catalytic metal chalcogenide nanoparticles, potentially providing more active sites for I₃⁻ reduction.

The rGO sheets also form highly conductive networks that connect

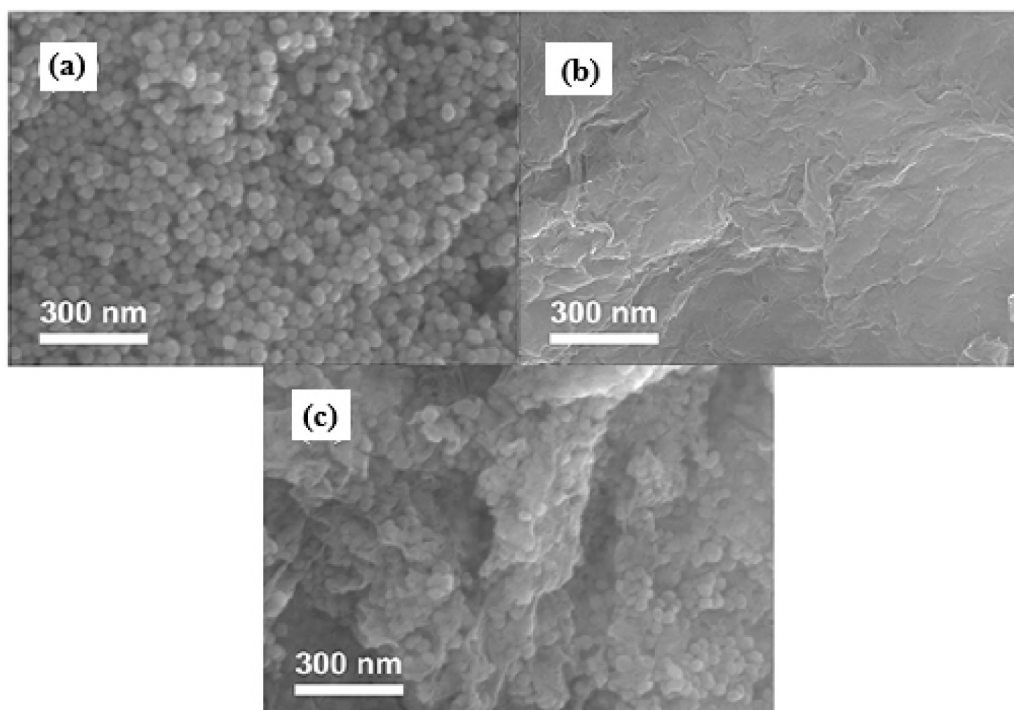


Fig. 7. Field-emission scanning electron micrographs of (a) α -Fe₂O₃, (b) rGO and (c) rGO/ α -Fe₂O₃ composites. Adapted under a Creative Commons license [196], Copyright (2022), open access.

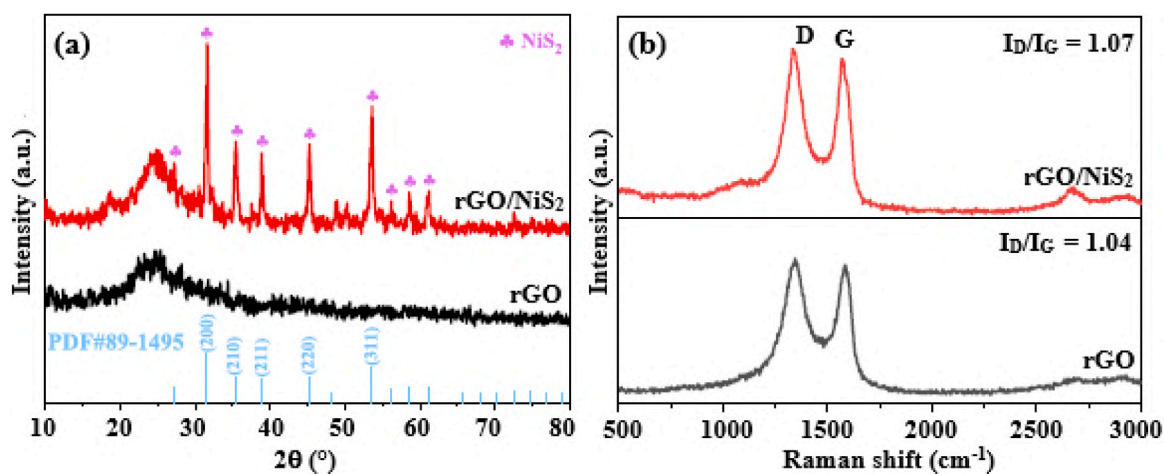


Fig. 8. (a) XRD diffractograms and (b) Raman spectra of pristine rGO and rGO/NiS₂ composites. Adapted from [205], Copyright (2023), with permission from Elsevier.

the metal chalcogenide nanoparticles and provide additional electron transport pathways. This reduces the charge transfer resistance (R_{ct}) at the counter electrode/electrolyte interface, e.g., as shown in the Nyquist plots from electrochemical impedance spectroscopy (EIS) analysis (Fig. 9(a)) [201], by the smaller diameter of the semicircle in the high-frequency region. This, in turn, facilitates the rapid transfer of electrons for catalyzing I_3^- reduction. Thus, when compared to Pt (0.83 Ω), the smaller R_{ct} (0.79 Ω) observed for the rGO/Ni₁₂P₅ composite indicates an increased electrocatalytic ability for I_3^- reduction due to the rapid charge-transfer process. Also, since the intercept of the semicircle in the high-frequency region with the real axis is numerically equal to the series resistance (R_s), largely affected by film adhesion to the substrate; the smaller R_s (11.56 Ω) of rGO/Ni₁₂P₅ than that of Pt (12.13 Ω) might have originated from the strong adhesion of the composite film to the substrate.

The electrocatalytic activity of the counter electrode materials for I_3^- reduction has been evaluated using cyclic voltammetry (CV), and compared with the Pt reference curve, consisting of two pairs of redox peaks. In Fig. 9(b) [201], the redox peaks at a relatively high potential correspond to the oxidation and reduction peaks of I_3^-/I_2 , while those at a relatively low potential correspond to the oxidation and reduction peaks of Γ/I_3^- . Since electrons from the external circuit play a prominent role in reducing I_3^- to Γ during an electrochemical process, the redox peaks at a relatively low potential represent the electrocatalytic capabilities of the counter electrode. Also, since the magnitude of the peak current density (J_p) and peak-to-peak separation potential (ΔE_{pp}) are correlated to the capacity of the counter electrode to transfer electrons for reducing I_3^- species and the reversibility of the redox reaction, respectively, the higher J_p and smaller ΔE_{pp} observed for rGO/Ni₁₂P₅ indicate its faster reduction reaction kinetics and better electrochemical

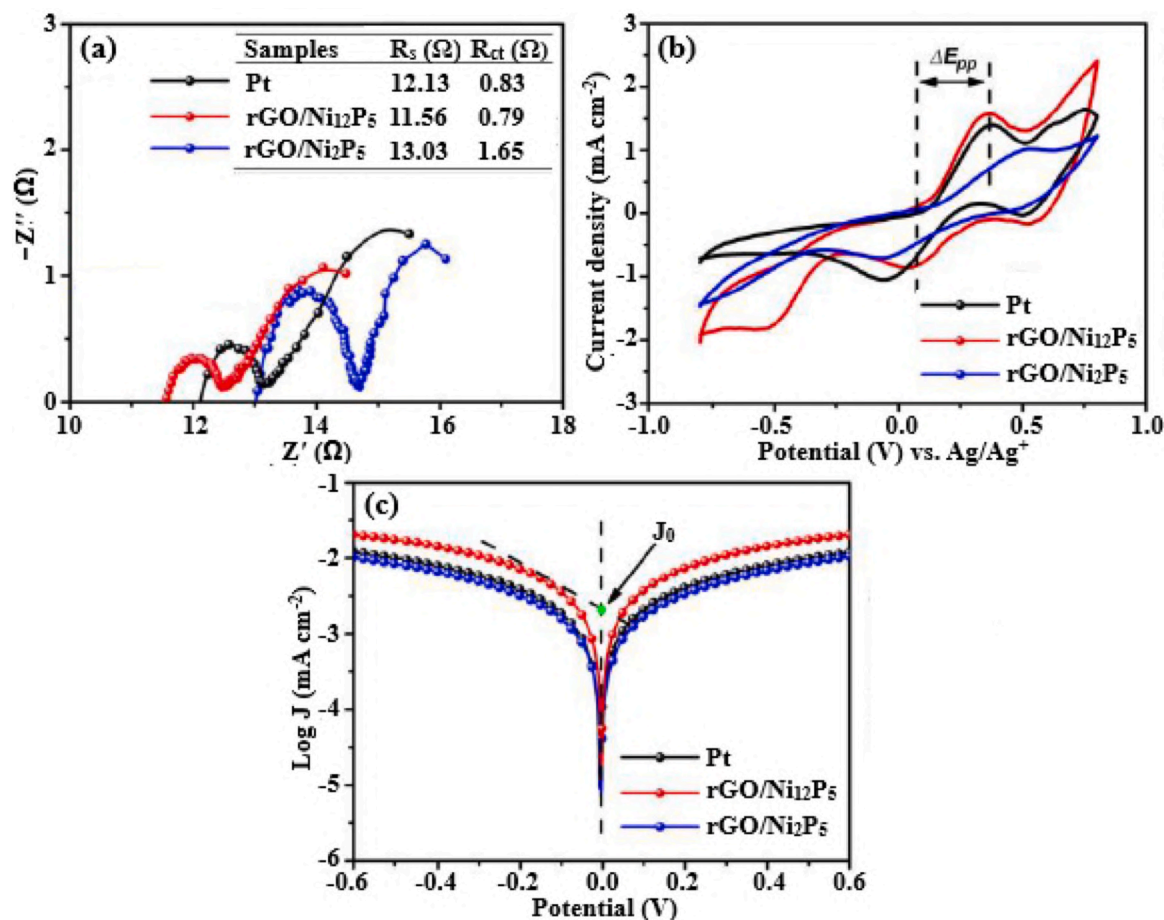


Fig. 9. (a) Nyquist plots, (b) cyclic voltammograms and (c) Tafel polarization curves of rGO/Ni₂P₅, rGO/Ni₁₂P₅ and Pt counter electrodes. Adapted from [201], Copyright (2020), with permission from American Chemical Society.

reversibility than those for Pt and rGO/Ni₂P₅. Therefore, the rGO/Ni₁₂P₅ composites exhibited outstanding electrocatalytic activity and faster response rates than those of Pt and rGO/Ni₂P₅. In addition, the appearance of a larger integral area on the CV curve of rGO/Ni₁₂P₅ composites compared to those of Pt and rGO/Ni₂P₅ demonstrates the potential of the rGO backbone to induce additional electrochemical processes, which ultimately enhance the electrochemical capacity of the Ni₁₂P₅ counter electrode. Thus, the competitive electrocatalytic activity of rGO/metal chalcogenide composites could make them effective alternatives to Pt counter electrodes in future research.

The electrocatalytic activity for I₃⁻ reduction has also been evaluated from the Tafel polarization curves by determining the exchange current density (J_0) in the Tafel region, from the intersection of the tangent of the cathodic branch and the equilibrium potential line (Fig. 9(c)), according to Eq. (1) [201]:

$$J_0 = \frac{RT}{nFR_{ct}} \quad (1)$$

where R is the universal gas constant, T is the absolute temperature, n is the number of electrons involved in the electrochemical reduction of I₃⁻, F is Faraday's constant, and R_{ct} is the charge transfer resistance. J_0 is correlated to the rate of electron transfer between the electrode and the redox species, and it serves as an indicator of the electrocatalytic activity of a counter electrode. From Fig. 9(c), the steeper the slope of the cathodic branch in the Tafel zone, the greater the J_0 and the higher the catalytic activity of a material. Hence, the rGO/Ni₁₂P₅ composite exhibited the largest J_0 in the Tafel zone, followed by Pt and rGO/Ni₂P₅. This was consistent with EIS data, which showed a decrease in R_{ct} in the order from rGO/Ni₂P₅ (1.65 Ω), Pt (5.42 Ω) to rGO/Ni₁₂P₅ (0.83 Ω). A

small R_{ct} is desirable since it enables a large number of electrons to be transferred through the counter electrode/electrolyte interface. Therefore, when compared to Pt and rGO/Ni₂P₅ counter electrodes, the rGO/Ni₁₂P₅ composite counter electrode (with smaller R_{ct} and larger J_0) displayed higher electrocatalytic activity, demonstrating the effectiveness of the composites in reducing I₃⁻.

As a consequence, DSSCs based on the rGO/metal chalcogenide composite counter electrode have surpassed the PCE of Pt reference devices, e.g., by ~60% [207,208], and in some cases reached up to ~90% [202,203] and ~97% [206] of the PCE of Pt-based control devices. Moreover, the rGO/metal chalcogenide-based devices outperformed the pristine metal chalcogenide devices, e.g., by ~196% [207], and pristine rGO devices, e.g., by ~168% [206]. The enhanced device performance can be attributed to the ability of the composite counter electrode to exploit both the high electrical conductivity of rGO and the high electrocatalytic activity of metal chalcogenides.

The introduction of highly stable rGO sheets into metal chalcogenides also enhanced the long-term stability of DSSCs, e.g., as revealed by the ability of rGO/NiSe₂- [199], rGO/MoS₂- [202] and rGO/NiS₂-based devices [205] to maintain above 95% of the original PCE after storage for 60, 10 and 30 days, respectively. Additionally, no noticeable changes in J_p and ΔE_{pp} appeared in the CV curves of the composite after 10000 cycles at a scan rate of 10 mV s⁻¹ (Fig. 10 (a)), while also the R_{ct} showed only a slight increase by ~7% (Fig. 10 (b)) [206], under the same conditions, demonstrating the robust electrochemical stability of the composite counter electrode. This was consistent with similar studies [27,108,200,202], which reported the fabrication of rGO/metal chalcogenide composite counter electrodes with superior electrochemical stability to their individual constituents. The excellent electrochemical

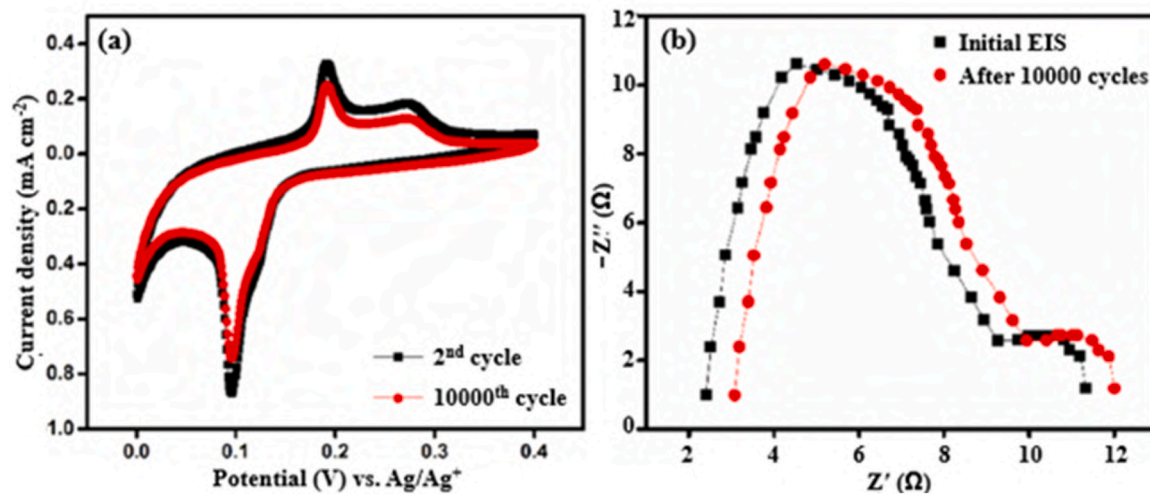


Fig. 10. (a) Cyclic voltammograms and (b) Nyquist plots of the rGO/CoNi₂S₄ composite (initial and after 10000 cycles). Adapted from [206], Copyright (2020), with permission from Elsevier.

stability of the composite electrode and long-term stability of the device are primarily owing to the presence of residual oxygen functionalized groups in rGO, which allows for the tight chemical anchoring of metal chalcogenide nanoparticles on the highly stable rGO sheet surface. This enables the rGO sheets to prevent the agglomeration and corrosion of counter electrode materials, while also the metal chalcogenide

nanoparticles prevent the restacking of rGO sheets.

6.3. Reduced graphene oxide/perovskite nanocomposites

Perovskite materials, such as La₂CrFeW₆ [191] and SSFC [209], have been recently integrated with rGO, and used as counter electrode

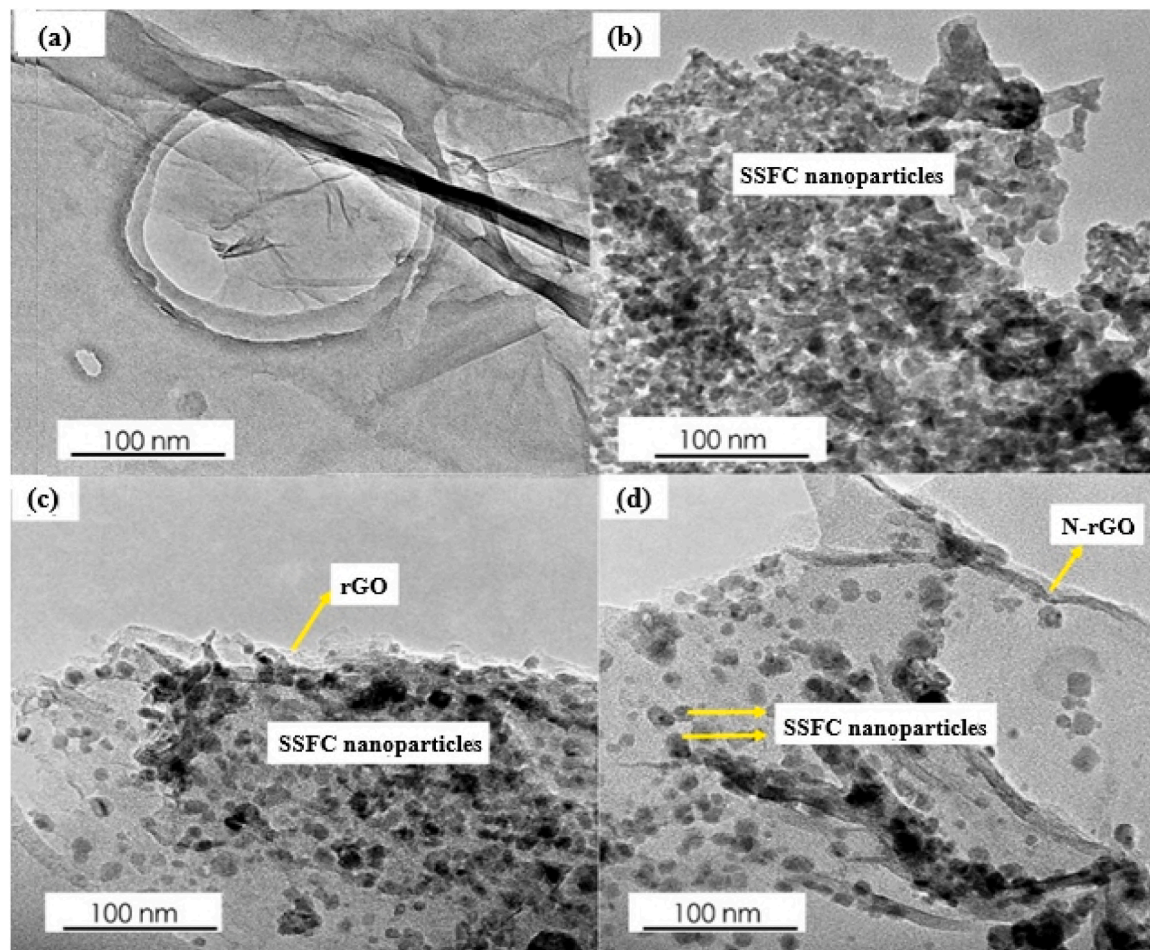


Fig. 11. Transmission electron microscopy images of (a) rGO, (b) SSFC, (c) rGO/SSFC and (d) N-rGO/SSFC. Adapted under a Creative Commons license [209], Copyright (2023), open access.

materials in Pt-free DSSCs. Among other merits, this enables the rGO sheets to help minimize perovskite nanoparticle aggregation, while at the same time, the perovskite nanoparticles help to prevent the restacking and aggregation of rGO sheets. For example, the recent introduction of wrinkled and folded rGO nanosheets (Fig. 11 (a)) into agglomerated SSFC perovskite nanoparticles of diameter ~ 24 nm (Fig. 11 (b)) led to the formation of well-dispersed and evenly decorated SSFC nanoparticles on the rGO (Fig. 11 (c)) and N-rGO nanosheet surfaces (Fig. 11 (d)) [209]. This ultimately renders the composite counter electrode with a larger surface area capable of enhancing the electroactive sites for the effective reduction of I_3^- .

Simultaneously, the rGO nanosheets provide the counter electrode with additional electron transport pathways, which lower the R_{ct} , and hence suppress recombination, as illustrated by the pronounced quenching of PL intensity in Fig. 12 [209]. It is interesting to note that recombination suppression through compositing was beneficial to both components and this suggests favourable chemical interactions between them. This enables the fast transfer of electrons from an external circuit to the electrolyte, which, in turn, catalyzes the reduction of I_3^- . The N-doped rGO composite is noteworthy for its relatively outstanding quenching performance of PL (Fig. 12 (b)). Consequently, this has led to the fabrication of rGO/perovskite composite-based devices with high PCEs, e.g., of $\sim 7\%$ [209] and $\sim 10\%$ [191], which not only outperformed the Pt-based reference device by $\sim 20\%$ [209] and 39% [191], but also the pristine SSFC and rGO devices by ~ 64 and 102% , respectively [209]. This demonstrates the potential of rGO/perovskite composites for use as Pt-free counter electrode materials in future DSSCs.

7. Conclusions and perspectives

When compared to commercially available crystalline silicon solar cells with a PCE of $>26\%$, the commercial application of DSSCs continues to be hampered by their low PCE ($\sim 15.2\%$) mainly due to the shortcomings of traditional electrode materials, i.e., TiO_2 and Pt. Among other issues, TiO_2 has a relatively low visible region transparency, which restricts the passage of more light into the DSSC. In addition, the wide band gap of TiO_2 (~ 3.2 eV) permits only UV light absorption, and also provides a large energy barrier that causes poor electron transfer at the dye/semiconductor interface. This causes the recombination of photo-generated electrons with oxidized dye molecules and I_3^- in the electrolyte. The small-sized mesoporous TiO_2 nanoparticles also have numerous defects and grain boundaries, which cause ineffective scattering of unabsorbed light back to the photoanode, poor light absorption, and poor electron transfer with high recombination. To circumvent

these drawbacks, TiO_2 has been used in combination with transparent and narrow or medium band gap materials to enhance visible region transparency, reduce the band gap and broaden the absorption spectrum to the visible region. This also helps to minimize the energy barrier at the dye/ TiO_2 interface, thereby facilitating the effective dissociation of photogenerated charge carriers and the subsequent transfer of photo-generated electrons with low recombination. Additionally, light-scattering and compact layers have been developed to ensure the maximum utilization of absorbed light by scattering it back to the photoanode, while also preventing direct contact between the electrolyte and the transparent electrode to suppress recombination. The integration of TiO_2 with highly conductive nanomaterials to provide additional electron transport pathways, as well as the post-synthesis treatment of TiO_2 to repair surface defects and improve electron transport, have also been employed to address the setbacks of TiO_2 . On the other hand, Pt, the traditional counter electrode material, is expensive due to its scarcity and has poor stability due to its poor resistance to corrosion from I_3^- in the electrolyte. This increases the cost of DSSCs and shortens their lifespan. As a result, several approaches such as elemental doping and developing Pt-based nanocomposites with comparable electrical conductivity and electrocatalytic activity, have been employed to improve device performance and stability.

Despite the above-mentioned efforts, the PCE and sustainability of TiO_2 - and Pt-based DSSCs have continued to be low. As a result, this has necessitated the development of TiO_2 - and Pt-free semiconducting materials, such as metal oxides, metal chalcogenides and perovskites, with comparable photovoltaic performance and high stability. However, on their own, these semiconducting materials tend to aggregate, giving rise to relatively low electrical conductivity and poor electrocatalytic activity, which reduces device performance. Therefore, these semiconducting materials have been recently integrated with highly conductive and sustainable carbon-based materials, particularly rGO, which is dispersible and compatible with low-cost solution synthesis. This also benefits from the advantages of rGO, such as its large specific surface area for more dye adsorption; wide and intense visible region absorption spectrum for more light absorption; high electrical conductivity for rapid electron transport with low recombination; high electrocatalytic activity for speeding up I_3^- reduction; excellent stability for prolonging device lifespan; and low-costs for reducing device cost.

From the reviewed recent studies, the use of rGO-based composites in devices based on the Γ/I_3^- redox couple and N719 dye has led to the fabrication of TiO_2 -free DSSCs with an optimum PCE of $\sim 10\%$, as well as Pt-free devices with a best PCE of $\sim 12\%$, i.e., reaching up to ~ 66 and 80% of the PCE of current state-of-the-art DSSCs based on TiO_2 and Pt electrodes. Hence, the continuous optimization of parameters in future

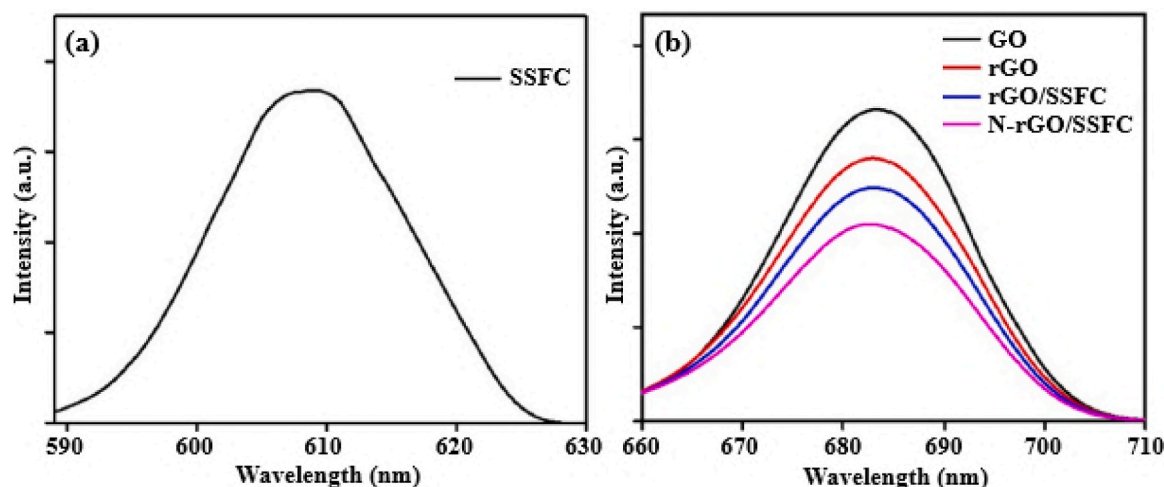


Fig. 12. PL spectra of (a) SSFC, and (b) GO, rGO, rGO/SSFC and N-rGO/SSFC. Adapted under a Creative Commons license [209], Copyright (2023), open access.

research, through approaches such as developing novel carbon-based nanocomposites, while also avoiding the dependence on scarce and costly traditional materials, has the potential to bridge the gap between emerging and traditional nanomaterials. This, if done, can conceivably lead to the development of next-generation DSSCs with a capacity to surpass the current optimum DSSC PCE (~15.2%) and approach the performance of crystalline silicon solar cells. This ultimately opens up the avenues for the commercialization of low-cost, efficient and sustainable devices. Therefore, this review has highlighted the recent progress in DSSC performance and sustainability achieved over the last five-year period (2020–2024) by fabricating TiO₂- and Pt-free electrodes, through incorporating rGO into semiconducting metal oxides, metal chalcogenides and perovskites. This is envisaged to contribute by helping to alleviate the current global issues, including the increasing energy demand, depletion of traditional energy sources, environmental pollution, global warming and climate change, through promoting the use of solar energy, a renewable energy source, which is abundant in nature, cost-effective and environmentally friendly.

CRedit authorship contribution statement

Conceptualization, E.M., E.T.M., C.M.M., T.S.S., A.Y. and D.P.; Writing – original draft, E.M., E.T.M., C.M.M., T.S.S., A.Y. and D.P.; Review and editing, E.M., E.T.M., C.M.M., T.S.S., A.Y. and D.P.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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