#### REVIEW



# A review of the development of graphene-incorporated dye-sensitized solar cells

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#### Abstract

To utilize abundant solar energy, dye-sensitized solar cells (DSSCs) have attracted researchers' attention due to many reasons, such as low production costs, easy fabrication methods, low toxicity of the materials, and relatively high-power conversion efficiencies. The use of expensive metal-dye complexes, the lack of long-term stability due to the use of liquid electrolytes, and the use of rare and expensive Pt as the CE are the major drawbacks preventing the large-scale production of DSSCs. However, recent studies showed alternative materials can be used to enhance the DSSC performance. The unique properties of graphene make it an ideal additive to improve the functions of all three components of DSSCs. Graphene's high optical transmittance and electron mobility are suitable to improve transparent conducting substrates and nanostructured wide bandgap semiconductor layers of the photoelectrode. Graphene quantum dots have a wide absorption spectrum and thus can be used as photosensitizers. High catalytic activity, high electrical conductivity, high corrosion resistance, and a larger specific surface area make graphene and its composites suitable for making CEs. In addition, graphene has been used to improve composite electrolytes intended for DSSCs. Considering all these facts, this article reviews the recent developments and applications of graphene-based materials in photoelectrodes, electrolytes and CEs and the possible uses of graphene to improve DSSCs.

Keywords Energy conversion, Photoanode  $\cdot$  Counter electrode  $\cdot$  Composite electrolyte  $\cdot$  Graphene  $\cdot$  Efficiency enhancement

# Introduction

Due to the ever-increasing complexity of the human lifestyle, the demand for energy and energy sources has increased exponentially in recent years. Therefore, different sources of energy such as hydropower, natural gases, petroleum, wind power, nuclear power, geothermal, solar, etc. have been exploited to satisfy rapidly increasing energy demand [1, 2]. Renewable energy sources are described as energy sources

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where the rate of replacing them with natural processes is greater than the rate of consumption. They include solar energy wind energy hydro energy and geothermal energy, etc. Most of the abovementioned renewable resources and their conversion process to usable energy forms such as electricity are clean and eco-friendly since they produce low to zero carbon emissions and are therefore less damaging to the environment compared to non-renewable sources like coal and oil. The rate of consumption of non-renewable energy sources is higher than the rate of replacing it by means of natural processes. They include fossil fuels and nuclear energy etc. These sources can be easily extracted and used, but they cannot be easily replenished. Energy conversion process of these release large amounts of greenhouse gases, and toxic and harmful waste products and have negative impacts on the environment. Despite their negative impacts on the environment, non-renewable energy sources continue to dominate the world's energy supply. There is an increasing trend of research and development to reduce the reliance on these problematic nonrenewable sources [3-5]. Harnessing solar energy to fulfil energy need is a sustainable and ecofriendly alternative.

# Solar energy

Out of all the energy sources available, the solar energy is a prominent source of energy because it is a reliable and costeffective source, highly abundant, environmentally friendly, and most importantly, a renewable source of energy. The use of solar energy is not a wonder because it is used by nature in the process called photosynthesis, which helps to sustain life on the planet [6].

# **Photovoltaic systems**

Photovoltaic (PV) cells directly convert sunlight into electricity. The most common PV cells in terms of cost, mass

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Fig. 1 Highest recorded efficiencies for different types of solar cells as of 2024 [7]

production, durability, and relatively high-power conversion efficiency are those manufactured using crystalline silicon, but many types of solar cells have emerged. Figure 1 gives the highest recorded efficiencies of different types of solar cells up to 2024 [7]. As shown in Fig. 1 multi-junction cells have recorded the highest power conversion efficiency (PCE) of 47.6% while that of single junction devices of GaAs and Si based cells are about 30% and 27%, respectively. In addition, recently developed organic inorganic perovskite solar cells have shown PCE of 25.7%. Dye-sensitized solar cells (DSSCs) have shown a maximum PCE of about 13–15%, thus the lowest of the cell types shown in Fig. 1 [6, 8, 9].

Figure 2 shows a comprehensive overview of published research papers in the field of dye-sensitized solar cells over past decades. For DSSCs, the number of published papers peaked about 10 years ago, papers referring to graphene have a more recent trend but also in that case the peak was in



Fig. 2 The number of publications from the period 1995-2023 containing the word, a) Dve + sensitized + solar + cell" in the title, abstract, or keywords. **b**) Dye + sensitized + solar + cells + graphene" in the title, abstract, or keywords from the period 2008-2023. Data source: Scopus (28th Jan. 2024)

2016. Although this seemingly declining interest for DSSCs and the low PCE the work on integrating graphene in this type of solar cell is intense and is expected to lead to important improvements of performance. This review will thus focus on the possibilities of improvements of DSSCs that are perceived by the introduction of graphene.

#### **Dye-sensitized solar cells**

A DSSC operates through a unique photovoltaic mechanism. In a DSSC, a semiconducting material (in general,  $TiO_2$ ) is coated with light absorbing dye. Once the sensitizer is irradiated, the electrons of the highest occupied molecular orbital (HOMO) are excited and get injected into the semiconducting layer, generating a photocurrent. The injected electrons flow through the semiconductor creating an electrical current in the external circuit. The electrolyte regenerates the dye by donating electrons to the photoexcited dye molecules and the electrolyte regenerates by capturing the electrons from the counter electrode (CE).

DSSCs are known for their low production cost, easy fabrication methods and promising future, in spite of a relatively low PCE and have gained much attention from researchers during the last three decades. DSSCs mimic the energy harvesting process in natural photosynthesis, and dye sensitization was first used in photography [10]. In 1976, Tsubomura first reported a dye-sensitized ZnO photoelectrochemical cell using a redox couple as an electrolyte [11]. The current generated by this process was very small because only a monolayer of dye was present on the rather flat photoactive surface. In 1985, Desilvestro reported that rough-surfaced TiO<sub>2</sub> with Ruthenium dye yielded higher photoconversion efficiency due to increased dye adsorption because of the large surface area of the nanostructured photoanode [12]. In all these studies, the light harvesting efficiencies were around 1% because a monolayer of dye was used, which was unable to harness the entire incoming solar energy. However, in 1991, a breakthrough discovery by O'Regan and Michael Gratzel reported a PCE of 7% in a DSSC using mesoporous TiO<sub>2</sub> and an iodide/tri-iodide redox couple [13]. Since then, research and development of the DSSCs have been accelerated and many new modifications have been done to the structure of the DSSCs to achieve higher and higher efficiencies of 10.4% in 1993 [14], 11.1% in 2006 [15], 12.5% in 2004 [16], in 2015 14.3% [8] and highest efficiency ever recorded for a DSSC of 15% in 2023 [9]. However, compared with traditional Si-based solar cells, DSSCs still have considerable drawbacks like low PCE, poor long-term stability, dye degradation, leakage of liquid electrolytes, and high sensitivity of polymer electrolytes to temperature variations, etc. To solve these problems and improve DSSC technologies, many recent studies have been carried out. More recently, the use of graphene and graphene-based materials in DSSCs has attracted much attention, and this development will be reviewed in detail below.

#### Action of a dye-sensitized solar cell

A traditional DSSC is composed of three main components: a working electrode (WE) or photoanode, an electrolyte, and a counter electrode (CE). The photoanode or working electrode consists of thin oxide layers coated on a transparent sheet of glass, first a very thin layer of conductive oxide, the two most common are indium tin oxide (ITO) or fluorine tin oxide (FTO) [17-19]. A nanostructured wide-bandgap semiconductor material (such as TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO or their composites) is coated on top of the conductive layer. This semiconductor layer absorbs the photosensitizer (ruthenium dye complexes) in order to allow photogeneration and transport of electrons. The electrolyte is a redox couple (in general, tri-iodide/iodide) for the regeneration of the dye molecules by transferring electrons collected from the CE during its operation cycle, and the electrolyte is sandwiched between the WE and CE [20-22]. .The CE is a glass sheet mainly coated with the catalyst (platinum), which allows the electrons to flow freely from the external circuit to the electrolyte and dye where regeneration and recombination reactions take place [23–25]. Figure 3 represents the basic components and working principle of a dye-sensitized solar cell [26].

#### Working electrode (WE)/photoanode

The working electrode or the photoanode of a DSSC consists of a transparent conductive oxide (TCO) layer coated on a glass substrate. On top of this TCO layer, a mesoporous wide-band gap nanocrystalline thin film is coated to which a layer of dye is adsorbed. The TCO layer should be highly transparent to visible light to maximize the cell efficiency by transmitting an optimum amount of light to the dye layer [27, 28]. In addition, it should exhibit high electrical conductivity to achieve efficient charge transport.

Typically, these TCO layers are deposited on glass or polymeric substrates. Glass substrates offer higher inertness, safety, transparency, and robustness for the DSSC, while polymer substrates offer lightweight, low-cost, and flexibility for the DSSC design. Various n-type semiconductor metal oxides are used as TCO layers, such as fluorine-doped tin oxide (FTO), indium-doped tin oxide (ITO), fluorine-doped zinc oxide, and aluminum-doped zinc oxide. However, FTO and ITO fulfill common industrial standards as they can easily be deposited on soda-lime glass substrates [29, 30]. Layer deposition techniques include atomic layer epitaxy [31], chemical vapor deposition (CVD) [32], and spray pyrolysis **Fig. 3** Schematic representation of the components and of the basic operating principle of a DSSC



deposition (SPD) [33–35] which are the most common and widely used techniques.

The nanocrystalline semiconductor thin film provides the active surface area for dye absorption and provides the route for electron transport from excited dye molecules to the TCO current collector (substrate) via injecting electrons into the conduction band of the semiconductor thin film. The utilization of porous nanostructured thin film enables a larger surface area for dye adsorption [36, 37]. The thickness of the semiconductor thin film also plays a critical role in dye adsorption. The larger the thickness of the film, the larger the amount of dye adsorbed [38, 39]. However, the higher thickness does not mean the cell can achieve higher efficiency because as the layer thickness increases, the injected electrons will have to travel a greater distance inside the film. This leads to an increase in recombination and an increase in the resistance for the electrons to move toward the TCO layer. Therefore, the layer should be at its optimum thickness to achieve a higher efficiency as well as minimize the recombination process.

Typically, nanostructured semiconductor thin films intended for DSSCs consist of particle sizes in the range of 13–25 nm [40–42] with varying layer thickness from 1 to 15  $\mu$ m [43]. The electron transport rate inside this semiconductor thin film depends on the morphology, crystallinity, and surface area of the material [27]. Researchers have designed and developed a variety of materials such as nanorods, nanotubes, nanowires, nanoflowers, and tetrapods to fabricate this semiconducting layer [44–47]. The most common wide-bandgap semiconductor oxides used in fabricating thin films for DSSCs are TiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> [48–51]. Dominant film preparation methods include spin coating [52–54], doctor-blade method [55, 56], screen printing [57], and spraying technique [58, 59].

Remarkable cell stability for DSSCs can be attained by using improved photoanodes and electrolytes. In the study, Bella et al. [60] developed  $\text{TiO}_2$  micropillar-photoanodes by patterning them with the help of the standard soft lithography technique using a poly(dimethylsiloxane) stamp. The authors reported high stability on prolonged aging over 2000 h at 50°C for gel polymer electrolyte-based DSSCs.

Compared to other semiconductor oxides, titanium dioxide shows excellent stability in visible irradiation conditions and can perform well in extreme conditions such as high temperatures, etc. Being non-toxic, widely available, and economically friendly make TiO<sub>2</sub> a promising and leading material for the industrial manufacturing of DSSCs. TiO<sub>2</sub> has three crystalline forms, namely anatase, rutile, and brookite. Both anatase and rutile phases are tetragonal in shape, in which Ti<sup>4+</sup> is six-fold coordinated to oxygen atoms. The main difference between these two structures is the position of the oxygen atoms. The anatase phase has a smaller average distance between Ti<sup>4+</sup> atoms compared to the rutile phase; this makes the anatase phase less thermodynamically stable [61]. Brookite phase is not widely abundant, and due to the difficulty in producing, it is not considered as a suitable material to fabricate DSSC photoanodes. The bandgap  $(E_{o})$  of anatase is 3.2 eV at 388 nm, and bandgap of rutile is 3.0 eV at 413 nm [62, 63]. Due to its higher bandgap and well-matched position of the conduction band, to the excited electron level of the dye molecules, the anatase phase is more favorable for DSSC applications. The high dielectric constant of anatase TiO<sub>2</sub> ( $\varepsilon = 80$ ) prevents the recombination of injected electrons with oxidized dye molecules, and the high refractive index of anatase  $TiO_2$  (n = 2.3) provides higher diffuse scattering of incident light inside porous semiconductors enhancing the optimum light absorption [64, 65].

#### Photosensitizer/dye

In a typical DSSC, the photosensitizer or dye is the photoactive material, and the cell can produce electricity once it is sensitized by light. The dye's light harvesting efficiency determines the DSSC's overall final efficiency. The main function of dye is to absorb photons from incident light and inject the excited electrons into the conduction band of the semiconductor thin film. An efficient dye should have the following properties [66, 67].

- I. Absorption spectra of the dye should be as broad as possible even covering UV-Vis and near-IR regions.
- II. The HOMO level of the dye should be at a lower energy level than the redox potential of the electrolyte and the lowest unoccupied molecular orbital (LUMO) level of the dye must be sufficiently high for efficient charge injection to n-type semiconductor.
- III. The hydrophobic nature of dye to enhances the longterm stability of the cell.
- IV. Availability of suitable co-absorbents like carboxylic acid (-COOH), phosphoric acid(-H<sub>2</sub>PO<sub>3</sub>), or sulfonic (-SO<sub>3</sub>H) acid to prevent dye aggregation over the TiO<sub>2</sub> surface.

Considering those factors, scientists have developed two main dye groups, namely, metal complex sensitizers and metal-free organic sensitizers. Metal complex sensitizers are dyes based on Ru [68, 69], Zn [70], Os [71], Pt [72], Cu [73], and Fe [74] have been potential candidates for DSSC applications. These photosensitizers contain a central metal ion with ancillary ligands having at least one anchoring group ( Fig. 4) [61]. Metal-free organic sensitizers are based on indoline dyes [75, 76], coumarin dyes [77], carbozole dyes [78] and tetrahydroquinoline dyes [79]. These metal-free organic sensitizers present several advantages over metal dye complexes, including being less expensive, easy adjustability of their properties, and high absorption. However, the performance of these organic dye complexes is relatively low when compared with metal complexes [80].

#### Electrolyte

The electrolyte is one of the most important components of a DSSC. The electrolyte is responsible for inner charge transport between electrodes and contains a redox couple (typically, tri-iodide / iodide) for the recovery of the dye and regeneration of the electrolyte during the operation. It is sandwiched between the photoanode and the CE. The efficiency of a DSSC is mainly governed by three basic factors: short-circuit current density  $(J_{\rm sc})$ , open-circuit voltage  $(V_{\rm oc})$  and the fill factor (*ff*). All these parameters are significantly affected by the properties of the electrolyte in the DSSC. For instance, the  $J_{\rm sc}$  is affected by the transport of the redox couple components of the electrolyte, the  $V_{\rm oc}$  can be affected by the redox potential of the electrolyte, and the fill factor can be affected by the diffusion of the charge carriers in the electrolyte and charge transfer resistance between the electrolyte/electrode interface [20]. To obtain maximum efficiency from a DSSC, an electrolyte should have the following properties:

- I. Should have high ionic conductivity in particular redox species shuttles between WE and CE
- II. The redox couple should be able to regenerate dye efficiently. Redox potentials should be compatible with the respective Fermi levels of the photoanodes.
- III. Should be long-term chemical, thermal and electrochemical stable.
- IV. Should be noncorrosive towards DSSC components and should provide good interfacial contact between the WE and CE.
- V. Absorption spectra of the electrolyte should not overlap with the dye (especially for back-side illumination and tandem structure).

By considering the above key factors, researchers have developed three main kinds of electrolytes: solid electrolytes, liquid electrolytes, and quasi-solid-state electrolytes (gel polymer electrolytes). Typical liquid electrolytes are easy to prepare, and they provide high ionic conductivity and better interfacial contact at the electrode-electrolyte interface. DSSCs fabricated with water-based liquid electrolytes showed some appreciable results [81, 82]. However, evaporation and leakage of the liquid components during long-term usage, ineffective sealing ability, and corrosion of the electrodes make the DSSC prepared with liquid





electrolytes to degrade in performance over time. However, as of today, a maximum efficiency of 14% for a DSSC has been achieved using liquid electrolytes [8, 83]. The use of solid electrolytes helps to overcome these problems because of their long-term physical and chemical stability but poor ionic conductivity and difficulty in improving charge transport properties researchers have focused on quasi-solid-state electrolytes (including gel polymer electrolytes) [84]. They are a compromise of the positive and negative effects of liquid and solid electrolytes, and offer better ionic conductivity, better sealing ability, and better long-term stability, and minimize the evaporation and leakage of liquid components. For instance, improved electrolytes for DSSCs using self-standing quasi-linear polymer electrolyte membranes reported 93% PCE retention after 500 h aging [81].

#### Counter electrode (CE)

The CE completes the electron transfer process from the photoanode to the electrolyte via an external circuit. The functional efficiency of the CE has a huge impact on the overall performance of the DSSC. An ideal CE should have high electrical conductivity, better long-term stability, and high electrocatalytic activity. Platinum is a perfect CE material for tri-iodide/iodide redox electrolyte systems. However, due to the higher cost of platinum and limited availability, large-scale manufacturing of the DSSCs becomes a huge problem, and research is needed to find low-cost, highly abundant materials with good electrical conductivity to be used as CEs. In this regard, carbon-based materials such as graphene, carbon nanotubes, and nanorods stand out as novel materials due to their very promising characteristics.

#### Working principle of a DSSC

The working process of a DSSC differs substantially from that of first- and second-generation solar cells as it is closely related to natural photosynthesis, where light absorption and charge transfer are carried out by different substances. There are five major steps involved in the operation of a DSSC. Figure 5 depicts a schematic diagram to represent the working principle of a DSSC [85].

There are 5 major steps involved in the process of conversion of light into electrical energy. Once the DSSC is illuminated by light, photons are absorbed by the dye molecules and electrons are get excited into LUMO from HOMO (Excitation).

$$S + hv \to S^* \tag{1}$$

Then, these excited electrons are injected into the CB of nanocrystalline  $TiO_2$  and the dye becomes oxidized (Injection).



Fig. 5 Schematic representation of the basic operating principle of a DSSC

$$S^* \to S^+ + e^- (\text{TiO}_2) \tag{2}$$

These excited electrons are diffused through the CB of nanocrystalline  $TiO_2$  and flow toward the TCO layer. These photogenerated electrons travel through an external circuit to generate electrical energy (Energy generation).

$$e^- + \text{TiO}_2(\text{CB}) \rightarrow \text{TiO}_2 + e^-(\text{CB}) + \text{electrical energy}$$
 (3)

At the same time, oxidized dye molecules regenerate by accepting electrons from the reduced redox couple (Regeneration of the dye).

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \tag{4}$$

Finally, the oxidized redox couple regenerates at the cathode by accepting electrons from the cathode (Electron capture).

$$I_3^- + 2e^- \to 3I^- \tag{5}$$

In the meantime, as this energy generation happens, recombination reactions also occur, which will result in a degradation of the energy generation rate of the DSSC. In Fig. 3, step 6 represents these recombination reactions. Three main types of recombination can occur inside a DSSC:

- I. Electron recombination by donating electrons to oxidized dye rather than going through an external circuit,
- II. Electron recombination by donating electrons to oxidized redox couple and
- Relaxation of the excited dye molecules to the ground state via a nonradiative decay process.

These recombination reactions are disadvantageous when enhancing the performance of a DSSC. New materials have to be found and research has to be done to improve DSSC properties [23].

#### Graphene

Graphene is a novel multi-functional material that is just a single atom thick and arranged in a hexagonal honeycomb lattice structure with sp<sup>2</sup>-bonded carbon atoms. Graphene has gained researchers' attention due to its electrical, physical, and chemical properties, including higher conductivity, transport, chemical inertness, thermal conductivity, optical transmittance, and hydrophobicity at the nanometer scale [86, 87]. Since its discovery in 2004, graphene has been one of the most extensively studied materials in the last decade [88]. Due to their groundbreaking discovery and work on graphene, scientists Andre Geim and Konstantin Novoselov won the 2010 Nobel Prize in Physics [89]. First, graphene was extracted using micromechanical cleavage, and this method allows easy production of high-quality graphene crystallites [88]. Graphene is considered a zero-bandgap semiconductor, and its unique properties produce unexpectedly high opacity for an atomic monolayer with a very low absorption ratio of visible light [90]. Exceptional electrical properties of graphene have attracted future electronic applications such as ballistic transistors, field emitter transistors (FET), integrated circuits (IC), and transparent conductive electrodes for applications such as solar cells, batteries, and sensors. Due to its high electron mobility and low Johnson noise, it can be utilized in the channel of FETs. Due to its high electrical conductivity and high optical transparency, graphene is a suitable candidate for transparent conducting electrodes, which are used in dye-sensitized solar cells, electrochromic devices, battery electrodes, organic photovoltaic cells (OPC), and organic light-emitting diodes (OLED) [91].

Typically, graphene is characterized by its number of layers as very few-layer graphene (vFLG, 1-3 layers of carbon), few-layer graphene (FLG, 2-5 layers), multi-layer graphene (MLG, 2–10 layers), or graphene nanoplatelets (GNP, stacks of graphene sheets that can consist of multiple layers). However, in addition to carbon layers, graphene comes in different commercial forms: graphene oxide (GO, a compound of C, O, and H), reduced graphene oxide (rGO, less O and H, more C), graphene powders and pastes, graphene nanoplatelets (with a thickness between 1 and 3 nm and lateral dimensions ranging from 100 nm to 100 microns), and functionalized graphene, which adds elements to the surface or edges of the graphene for some applications [92]. Figure 6 represents different forms of functionalized graphene available today [93]. Graphene quantum dots are emerging as a suitable material to enhance efficiency in DSSCs [94].

#### Preparation of graphene and functionalized graphene

Many advanced methods for synthesizing graphene have been developed since its discovery in 2004 by Geim and Novoselov using the now famous as Scotch tape method. The main concern in synthesizing graphene is producing samples with low defect density and high carrier mobility. However, there is currently no advanced method to synthesize such high quality as early mechanical exfoliation. However, this mechanical exfoliation is much more timeconsuming and limited to small-scale production [95]. However, for graphene to be used in industrial and large-scale applications, methods for producing it with high quality at a low-cost must be developed. These synthesis processes should be highly reliable, scalable, and cost-effective, with high graphene yields [96–98].

There are two main approaches in synthesizing graphene: top-down methods and bottom-up methods [99, 100]. The Most common top-down methods are mechanical exfoliation [101], arc discharge [102], and liquid phase exfoliation [103, 104]. These methods destroy large chunks of precursors such as graphite and other carbon-based precursors to form nanoscale graphene. Generally, these top-down methods are highly scalable and produce very high-quality graphene, but the difficulty in producing products with consistent properties is a disadvantage of the method. In bottom-up method synthesizes graphene by combining other smaller constitutes materials. Most common bottom-up methods include chemical vapor deposition (CVD) [105, 106], epitaxial growth [107, 108], template route synthesis [109] and total organic synthesis [110]. Even though bottom-up methods produce very high-quality, defect-free graphene, the high production cost and need of highly advanced instrumentation and synthesizing techniques are major disadvantages when using them in commercial applications [85]. Synthesis methods of graphene are illustrated in Fig. 7, and Table 1 represents the comparison of the properties of graphene synthesized using different synthesizing methods [81].

### **Discussion and review**

#### Graphene for dye-sensitized solar cells

The United States National Research Council (USNRC) evaluates the abundance of all types of minerals found in the earth's crust. Among this list, 11 critical elements have emerged showing a huge demand by manufacturing industries, including copper, gallium, indium, lithium, manganese, niobium, some platinum group metals, and some rare-earth elements, as assessed by a criticality matrix, which is shown in Fig. 8 [117].

**Fig. 6** Illustration of structures of different forms of graphene: **a**) graphene oxide (GO), **b**) Pure graphene, **c**) functionalized graphene, and **d**) reduced graphene oxide (rGO)

















For the growth of the solar cell and semiconductor industries, minerals such as silicon, tellurium, gallium, platinum, and indium are critically important. Among these critical elements, platinum and indium are found to be the most important minerals from the point of view of their future availability, exhaustion of natural resources, economic and environmental acceptability, and some geopolitical concerns as well. Therefore, it has become a priority to find low-cost,

Table 1 Comparison of graphene synthesis methods. Shows the typical number of layers produced, size of graphene layers (largest dimension) and mobility on  $Si/SiO_2$ 

Method	Layers	Size	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
Exfoliation	1 to 10+	1 mm [111]	15000 [112]
Thermal SiC	1 to 4	50 µm [113]	2000 [100]
Ni-CVD	1 to 4	1 cm [114]	3700 [101]
Cu-CVD	1	65 cm [115]	16000 [ <b>116</b> ]

highly abundant, and organic substitutes to power up the solar cell industry. For example, indium tin oxide (ITO) has been used in manufacturing electronic components, transparent electrodes, and the fabrication of solar cells. Another important metal is platinum. It is more valuable than gold and is used in catalytic technologies, chromotherapy, electronic component manufacturing, and many solar cell applications as the CEs. Therefore, researchers are currently aiming at producing low-cost, highly abundant substitutes for these expensive and rare metals.

# Graphene-based transparent conducting electrodes in DSSCs

Transparent conducting electrodes (TCEs) are required for DSSCs and other electronic device components such as electrochromic glasses, LCDs, and touchscreens. Indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) are widely used TCE materials due to their high optical transparency, conductivity, and low sheet resistance. However, due to its high cost, scarcity, and brittleness, both academia and industry have experimented with alternative TCE substitutes. One of the promising candidates is carbon-based materials such as graphene and carbon nano-tubes. Graphene, synthesized from carbon-based materials, which are one of the most abundant materials on the planet with no signs of scarcity or depletion. Graphene-based materials offer very high catalytic activity, close to that of platinum (> 90%), and they offer very high optical transparency and higher flexibility to fabricate devices. Graphene and graphene oxide layers can be used to replace FTO and ITO thin films since these materials show high light transmittance and high electrical conductivity.

Li et al. [118] reported a sheet resistance of 2.1 k $\Omega$ /sq for single-layer graphene and 350  $\Omega$ /sq for 4-layer graphene with ~90% optical transparency at a wavelength of 550 nm. Therefore, both the optical transparency and resistance of the graphene decrease as the number of graphene layers increases. High optical transparency, low sheet resistance, and higher carrier mobility are critical factors when considering a suitable substrate to prepare photoelectrode for a DSSC. Therefore, graphene fits perfectly to develop as a transparent conductive electrode material [106].

Bae et al. [119] reported a sheet resistance of 30  $\Omega$ /sq at 90% of optical transparency for a 4-layer graphene film prepared by layer-by-layer method and a sheet resistance of 125  $\Omega$ /sq at 97.4% of optical transparency for CVD-grown monolayer graphene. Bonaccorso et al. [120] reported that the optical absorption of graphene is proportional to the number of layers, each absorbing ~2.3% over the visible spectrum, and with 4 layers of graphene, an optical transmittance of ~90% can be achieved. In 2008, Wang et al. [121] were the first to report on using graphene materials as TCE in a DSSC. The film was fabricated using exfoliated graphite oxide, followed by thermal reduction. The obtained film



**Fig. 8** Criticality Matrix derived from the NRC Study "Minerals, Critical Minerals, And the U.S. Economy" [117]

exhibits a high conductivity of 550 S cm<sup>-1</sup> and transparency of more than 70% over the 1000–3000 nm wavelength range. With this TCE, the authors achieved a PCE of 0.26% under stimulated solar light of intensity 98.3 mW cm<sup>-2</sup>. In another study reported by Selopal et al. [122] few layers of polycrystalline graphene were prepared by CVD and achieved an outstanding PCE of 2% under one sun irradiation (1.5 AM, 100 mW cm<sup>-2</sup>). This was the highest ever recorded efficiency for that kind of cell up to that time, using graphene as a TCE material. In another study, Roh et al. [123] prepared surface-modified FTO substrates with rGO sheets using the Langmuir-Blodget (LB) technique to decrease the charge recombination at the TiO<sub>2</sub>/FTO interface. By using graphene modified FTO substrates the surface resistance at the TiO<sub>2</sub>/FTO interface was reduced and they were able to achieve an excellent PCE of 8.44%. For a better comparison significant  $V_{oc}$ ,  $J_{sc}$ , ff and PCE values of the DSSCs prepared using different TCEs are tabulated in Table 2.

#### Graphene-based semiconducting layers in DSSCs

Materials such as mesoporous nanocrystalline TiO<sub>2</sub>, SnO<sub>2</sub>, and ZnO have been widely used as semiconducting materials in DSSC photoanodes. The dye molecules inject electrons into this layer, and electrons are then diffused to the current collector (e.g., FTO). However, a loss of these electrons can occur due to many reasons, such as high ohmic resistance of the semiconducting layer, recombination of these injected electrons with oxidized species of the electrolyte or dye molecules, etc., eventually results in the reduction of the PCE of the cell. Therefore, graphene materials have received a significant attention as a potential candidate to improve the photoelectrodes of DSSCs due to their promising characteristics, such as large specific surface area ~  $2.63 \times 10^3 \text{ m}^2 \text{ g}^{-1}$  [115], high optical transmittance in visible the region [128] and faster electron mobility of  $15,000 \text{ cm}^2$  $V^{-1}$  s<sup>-1</sup> [112]. Considering this fact, graphene-TiO<sub>2</sub> hybrid semiconducting films have been developed to improve the PCE of DSSCs by enhancing electron mobility and reducing electron-hole charge recombination. According to a study carried out by Fang et al. [129] different graphene-P25 (G-P25) nanocrystalline TiO<sub>2</sub> photoelectrodes have shown that with an increase of graphene oxide (GO) content, the porosity of the G-P25 photoelectrodes, the interfacial recombination resistances and short circuit current densities have increased. They also reported that the cell with the best performance showed an interfacial resistance of 15.12  $\Omega$  and PCE of 5.09% under one sun irradiation. Nanocrystalline SnO<sub>2</sub> has also been used in DSSCs as a potential candidate for replacing TiO2-based semiconducting layers. However, due to poor electron transfer rates, mobility, and dye absorption, SnO<sub>2</sub>-based photoanodes were unable to achieve the expected higher DSSC efficiencies. Basu et al. [130] addressed these drawbacks using a hybrid semiconducting layer such as TiO<sub>2</sub>/SnO<sub>2</sub>/graphene and achieved the highest PCE of 3.37% which was ~16% higher than cells made with photoanodes using only SnO<sub>2</sub>-TiO<sub>2</sub>. The PCE enhancement was attributed to the enhanced electron lifetime and reduced charge recombination in the hybrid TiO<sub>2</sub>/ SnO<sub>2</sub>/graphene heterostructure photoanodes, and it was confirmed by the transient photovoltage decay and electrochemical impedance spectroscopy. Another reason for the improvement of PCE was the enhanced dye-loading capacity of the hybrid photoelectrode, which was confirmed via UV-Vis-NIR spectroscopy [130]. Another study reported by Yang et al. [131] indicated two-dimensional (2D) graphene could be used as 2D bridges into nanocrystalline TiO<sub>2</sub> electrodes, which brought faster electron transport, lower recombination, and higher light scattering. This study also showed that the  $J_{sc}$  was increased by 45% without sacrificing the  $V_{oc}$ , and the total conversion efficiency was 6.97%, which was an enhancement by 39%, compared with the nanocrystalline titanium dioxide photoanodes. Chen et al. [132] reported the enhancement of the power conversion efficiency of a DSSC by reducing the charge recombination that occurs at the FTO/TiO<sub>2</sub> interface by using graphene functionalization. By using graphene to functionalize both TiO<sub>2</sub>/TiO<sub>2</sub> and FTO/TiO2 interfaces, the PCE of the cell was increased from 5.80 to 8.13%. The enhanced PCE was attributed to the improved charge transfer and delayed charge recombination

Electrode configuration	$V_{\rm oc}$ / mV	$J_{\rm sc}$ / mA cm <sup>-2</sup>	ſſ	PCE /%	References
Graphene/Ni grids	330	1.33	0.57	0.25	[124]
Graphene/FTO	700	1.01	0.36	0.26	[121]
Graphene/Pt grids	430	2.87	0.32	0.40	[124]
rGO/ZnO	390	2.59	0.45	0.45	[125]
Graphene	630	7.80	0.40	2.00	[122]
GNPLs/FTO	690	7.41	0.45	2.32	[126]
GLC/FTO	710	15.60	0.63	6.92	[127]
rGO/FTO	680	18.95	0.65	8.44	[123]

\* Ni = Nickel, GNPLs = Graphene nanoplatelets, GLC = Graphene-like carbon

open-circuit voltage ( $V_{oc}$ ), shortcircuit current density ( $J_{sc}$ ), fill factor (ff), and PCE of the DSSCs prepared using different graphene-based TCEss

Table 2 The values for the

achieved by graphene-functionalized interfaces in the PCE photoanode.

For the first time, Fang et al. [133] reported graphene quantum dot (GQD) assisted dye-sensitized TiO<sub>2</sub> photoelectrodes demonstrating that dye adsorption increased with the increase of GQDs while values of  $J_{sc}$ ,  $V_{oc}$ , and PCE decreased with the increase of GQDs. In that study, they were able to achieve a maximum  $J_{sc}$  of 14.07  $\pm$  0.02 mA  $\text{cm}^{-2}$  and PCE of 6.10 ± 0.01%, which were higher than the traditional TiO<sub>2</sub>-based DSSCs by 30.9% and 19.6% respectively. Fan et al. [134] reported on DSSCs fabricated using TiO<sub>2</sub> nanosheets (TiO<sub>2</sub>-NSs)/graphene nanocomposite films. A series of photoelectrodes for DSSCs were fabricated by varying the graphene weight percentage. This study was able to confirm that the PCE of a DSSC can be improved to a great extent upon graphene loading, and it was dependent on the loading amount of graphene. In this study, TiO<sub>2</sub>-NSs/graphene nanocomposite films with moderate loadings (<0.75 wt%) showed enhanced photoelectric conversion efficiency compared with their pristine TiO2-NSs counterparts. However, the study also stated that high graphene loadings (>0.75 wt.%) result in a decrease in PCE. Under optimal conditions, the PCE of the graphene (0.75 wt%) solar cell is 5.77%, which is higher than that of pure  $TiO_2$ -NSs cells (4.61%) by 25%. This PCE improvement was attributed to the reduction of electrode-electrolyte interfacial resistance, the reduction of charge recombination rate, enhanced light scattering, and the enhancement of charge transport because of the addition of graphene. The decrease of PCE at high graphene loadings (> 0.75 wt.%) was attributed to the shielding of light-harvesting dye molecules by graphene. For a better comparison  $V_{oc}$ ,  $J_{sc}$ , *ff* and PCE of the DSSCs prepared with graphene-based semiconducting layers are given in Table 3.

Pattarith. K et al. [143] have fabricated silver nanoparticle adhered RGO/Pt counter electrodes and TiO2 electrodes with RGO/Ag for photoanode in a DSSC. The highest efficiency, optimized cell in this study showed a PCE of 9.15% which was higher than the standard DSSC. They attributed the enhanced PCE of the cell to the improvement of dye loading, improvement of electronic conductivity for the photogenerated charge carriers and, prevention of the electron-hole recombination process. A study by Tang et al. [144] on optimized TiO<sub>2</sub> photoelectrodes with RGO shows that the cell was able to achieve a PCE of 11.8% which was much higher than the previously reported PCEs for graphene modified DSSCs. The improved efficiency was due to the enhanced scattering ability of the incident light and the increase of the surface area for dye loading. Krishnamoorthy et al. [145] developed a novel strategy to prepare NiS<sub>2</sub> microspheres interface with 2D graphene nanosheets for the use of photoanodes in DSSCs. This study showed that the NiS<sub>2</sub> /graphene hybrid photoanode achieved a PCE of 12.56% under standard irradiation conditions. They also mentioned that the improved photoanode displayed excellent electrocatalytic activity in the reduction of tri-iodide ions.

#### **Graphene-based electrolytes**

The main role of the electrolyte is to indirectly conduct electrons through the redox couple (e.g., tri-iodide/iodide) to regenerate the oxidized dye molecules. A good electrolyte

Table 3 The values for the
open-circuit voltage ( $V_{oc}$ ),
short-circuit current density
$(J_{sc})$ , fill factor ( <i>ff</i> ), and PCE
of the DSSCs prepared with
graphene-based semiconducting
layer photoanodes

Electrode configuration	$V_{\rm oc}$ / mV	$J_{\rm sc}$ / mA cm <sup>-2</sup>	ſſ	PCE /%	References
GO/ZnAl-MMO	370	4.46	0.34	0.55	[135]
ZnO/rGO	640	3.02	0.60	1.55	[136]
TiO <sub>2</sub> /SnO <sub>2</sub> /Graphene	650	9.03	0.58	3.37	[130]
GO/TiO <sub>2</sub>	720	9.80	0.53	3.70	[125]
GO/TiO <sub>2</sub>	710	8.98	0.70	4.46	[137]
N-TiO <sub>2</sub> /Graphene	710	15.38	0.46	5.01	[138]
GO/TiO <sub>2</sub>	616	10.28	0.64	5.09	[129]
TiO2-NSs/Graphene	606	16.8	0.57	5.77	[134]
GQD/TiO <sub>2</sub>	660	14.07	0.59	6.10	[133]
Ag/rGO/TiO <sub>2</sub>	730	14.08	0.66	6.87	[139]
Graphene/TiO <sub>2</sub>	690	16.29	0.62	6.97	[131]
rGO/TiO <sub>2</sub>	540	28.36	0.47	7.20	[140]
Graphene/TiO <sub>2</sub>	751	19.47	0.56	8.13	[132]
rGO/TiO <sub>2</sub>	630	25.02	0.54	8.51	[141]
Graphene/MoS <sub>2</sub>	820	15.82	0.71	8.92	[142]
Ag/rGO/TiO <sub>2</sub>	780	14.30	0.82	9.15	[143]
rGO/Graphene/TiO <sub>2</sub>	710	26.00	0.64	11.80	[144]
Graphene/NiS <sub>2</sub>	890	23.13	0.85	12.56	[145]

should be highly thermally, chemically, electrochemically stable, should have a high ionic diffusion coefficient, low vapor pressure, and be easy to seal without suppressing carrier transport. In this regard, gel polymer electrolytes have been used as novel electrolyte material. However, polymer electrolytes require organic solvents (e.g., EC and PC) to act as plasticizers, which makes the electrolyte more unstable at high temperatures and also increase the risk for leakage of these organic solvents. Therefore, carbon-based materials such as graphene, CNTs, and their derivatives have gained considerable attention from the scientific community [146] as promising additives to electrolytes to enhance their conductivity and long-term stability. The use of graphene in an electrolyte can be divided into two main categories, namely, using graphene as a minor additive and using graphene as a main constituent (>1 wt.%) [147]. However, the use of graphene materials in high concentrations may increase the electrolyte electronic conductivity and lead to a decrease in the PCE of the DSSC. Therefore, the most likely scenario is to use graphene materials as a minor additive to the electrolyte.

A research study carried out by Ahmed et al. [148] utilized graphene nanomaterials in ionic liquids as potential electrolytes for DSSCs. In this study, graphene, singlewalled carbon nanotubes (SWCNTs), and a mixture of graphene and SWCNTs were incorporated into the ionic liquid, 1-methyl-3-propylimidazolium iodide (MPII). The study showed a PCE of 0.16% for the electrolyte containing only MPII a PCE of 2.10% for the electrolyte containing graphene and MPII, a PCE of 1.43% for the electrolyte containing SWCNTs with MPII, and a PCE of 2.50% for the electrolyte containing a mixture of graphene and SWCNTs with MPII. The efficiency enhancement with added graphene and SWCNTs was attributed to the increase in charge transport in ionic liquids and the use of carbon materials as a catalyst for the electrochemical reduction of the redox couple (triiodide/iodide). A study by Lin et al. [149] used poly (ionic liquid)/ionic liquid/graphene oxide (poly(IL)/IL/GO) composite gel electrolytes containing poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide), 1-propyl-3-methylimidazolium iodide (PMII) and graphene oxide as the electrolyte for DSSCs without any volatile organic solvent. The study was able to show that the conductivity of the composite electrolyte was significantly increased by adding the appropriate amount of GO and also showed that the electrolytes containing GO exhibit higher PCE and better long-term stability compared to those without GO. According to these results, the DSSC with electrolyte, containing 2 wt.% GO showed a higher PCE of 4.83% under simulated 1.5AM solar spectrum irradiation, whereas the DSSC with graphene-free electrolyte showed a PCE of 1.46% under the same illumination. Another interesting study conducted by Byrne et al. [150] reported that the improved PCE of DSSCs with carbon-based electrolytes could be achieved by tuning the thickness of the  $TiO_2$  layer. SWCNT-based electrolytes showed increased PCE from 1.43 to 3.49%. For the mixture of graphene and SWCNTs, the PCE improved from 2.5 to 2.93%. The electrochemical impedance spectroscopy (EIS) demonstrated that the addition of these carbon-based nanomaterials into MPII significantly decreased the charge transfer resistance at the electrodes, and much better PCEs can be achieved with carbon nanomaterial-incorporated electrolytes compared to pure MPII-based DSSCs.

Khannam et al. [151] also demonstrated the advantages of using graphene added electrolytes in DSSCs. He incorporated GO into gelatin hydrogel and used it as an electrolyte in DSSCs. Overall, the study was concerned with identifying the effects of different GO concentrations in gelatin and the effect of NiO content on the PCE of a quasi-solid state DSSC. According to the study the DSSC fabricated using conventional TiO<sub>2</sub> showed a maximum PCE of 1.31%at an optimum concentration of 0.1% GO in gelatin as GO formed some networks with gelatin network and enhanced the charge transportation through gel electrolyte. The optimized NiO and TiO<sub>2</sub> hybrid photoanode (5% NiO) achieved a PCE of 4.02%. For the first time, Kowsari et al. [152] reported on the preparation of highly effective DSSC electrolytes by combining GO with ammonium-based ionic liquids. This study showed that the ionic liquid functionalized GO formed a molecular bridge for electron transfer in ionic liquid-based electrolytes and they were able to achieve a remarkable PCE improvement up to 8.33%. A study by Venkatesan et al. [153] reported on the preparation of GO nanofiller-based PEO and PVDF electrolytes for the fabrication of DSSCs. In this study, the effects of various concentrations of GO nanofiller-added electrolytes were studied. From this study, they were able to show that the incorporation of 1.5% GO nanofillers decreases the charge transfer resistance at the Pt counter electrode /electrolyte and increases the recombination resistance at the photoelectrode/electrolyte interface. The fabricated quasi-solid state DSSC was able to achieve a PCE of 8.78% which was a significantly high value. Zheng et al. [154] demonstrated optimized strategies for synthesizing graphene-tailored polymer gel electrolytes in DSSC applications. The study reported that an increase in catalytic capability and shortened charge transfer length is due to the presence of graphene channels in 3D polymer gel electrolytes. These improvements have led to a superior power conversion efficiency of up to 9.1% for the fabricated quasi-solid state DSSC. All these results show that graphene and graphene-based materials such as GO, SWCNT, etc. can be incorporated into DSSC electrolytes as additives. The incorporation of these materials could enhance the performance of the DSSCs, as graphene materials could improve the ionic conductivity within the electrolyte and reduce the charge transfer resistance. Table 4 summarizes the results

**Table 4** The results ofpublished work on open-circuitvoltage ( $V_{oc}$ ), short-circuitcurrent density ( $J_{sc}$ ), fill factor(ff), and PCE of the DSSCsprepared by adding grapheneand graphene-based materialsinto the electrolyte as anadditive

Electrolyte configuration	$V_{\rm oc}$ / mV	$J_{\rm sc}$ / mA cm <sup>-2</sup>	ff	PCE /%	References
MPII ionic liquid	570	0.59	0.33	0.10	[155]
MPII ionic liquid	575	0.370	0.64	0.16	[148]
MPII/SWCNT	540	5.19	0.41	1.43	[148]
MPII/graphene	624	5.30	0.49	2.10	[148]
GQDs	410	16.95	0.32	2.23	[156]
MPII/graphene/SWCNT	594	7.32	0.44	2.50	[148]
PMII/graphene/SWCNT	640	7.89	0.58	2.93	[150]
PMII/SWCNT	711	7.35	0.67	3.49	[150]
GO/gelatin	750	7.68	0.70	4.02	[151]
Poly (IL)/PMII/GO	720	8.84	0.76	4.83	[149]
rGO/PMMA	870	9.83	0.63	5.38	[157]
GNPLs/PEG-PEO/PVDF-HFP	640	13.81	0.62	5.45	[158]
Graphene nanoribbons	760	9.98	0.76	5.75	[159]
PAA-CTAB/GO gel	687	13.74	0.63	6.35	[160]
Graphene nanoribbons/electrolyte	760	12.19	0.76	7.01	[159]
PAA-PEG/graphene	731	15.0	0.68	7.74	[161]
GO-HMA-TBAI/PMII-DMII	750	16.85	0.66	8.33	[152]
PEO/PVDF-GO	800	14.79	0.75	8.78	[153]
Graphene-PAA/PEG	740	17.80	0.69	9.10	[154]

\*MPII - 1-methyl-3-propylimidazolium iodide, PMMA – Poly methyl methacrylate, GO-HMA-TBAI – graphene oxide-hexa-methylene tri-butyl-ammonium iodide, DMII-1,3-dimethylimidazolium iodide, PVDF-HFP - Poly(vinylidene fluoride-co-hexafluoro propylene), PAA-CTAB - Poly(acrylic acid)-cetyltri-methylammonium bromide

from various studies carried out by incorporating graphene materials into the electrolyte as an additive.

#### **Graphene-based photosensitizers**

Photosensitizers play an important role in harvesting a spectrum of sunlight. The electrons from the excited dye molecules are injected into the semiconducting layer to create a photoinduced current. The most used photosensitizers are ruthenium-based complexes due to their wide absorption spectra from the visible to near-IR regions and excellent charge transfer properties. However, these complexes require multistep synthesis and contain heavy metals that are toxic, scarce, and expensive [125]. Therefore graphene, due to the wide absorption spectrum, which enables a single layer to absorb 2.3% of the incoming light [128], has been identified as a potential candidate as photosensitizer.

A review by Hagfeldt et al. [66] reported that researchers have synthesized over a thousand different types of dyes that can be used as sensitizers in DSSCs. Another interesting article by Mishra et al. [162] reviewed the advances in metal-free organic dyes and their technological aspects in DSSCs. Both these review articles indicated the necessity of finding a low-cost alternative to metal dye complexes, and an extensive amount of research has been done by both academia and industry in this regard. A study carried out by Ismail et al. [163] used a mangosteen dye as

a sensitizer with GO as a catalyst to improve the performance of DSSC. The research reported a modest efficiency enhancement from 0.31% for the dye that contained mangosteen only to 0.40% for the dye that contained both GO and mangosteen. The EIS data in this study showed that the GO helped to decrease the charge transfer resistance and increase the PCE of the cell. The study also demonstrated that GO can be used as a catalyst to create more photocurrent conversion pathways.

Metal organic frameworks (MOFs) have also been used as sensitizers in DSSCs due to their low-cost, high stability, biocompatibility, and superior light-harvesting properties. Kaur et al. [164] were inspired by this and developed a MOF-graphene composite photo-sensitizer for use in DSSCs. The cell was able to achieve a PCE of 2.3% and it was a significant improvement when compared with previous results obtained by Lee et al., a PCE of 0.26% [165]. According to recent theories, graphene materials have shown promise in hot injection [166] and multiple carrier generation [167] providing a way to exceed the Shokley-Quiessar efficiency limit in a DSSC [147]. Motivated by these findings, Yan et al. [168] were able to fabricate the first DSSCs with graphene quantum dots (GQDs) as photosensitizers. The device used GQD sizes ranging from ~1 to 30 nm and had an extinction coefficient of  $1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  which is higher than that of N719 dye. Another study reported by the same group [169] showed that the bandgap of GQDs can be tuned by varying the particle size, and that effect can be predicted theoretically through tight-binding calculations.

Based on another study, Ji et al. [170] reported an in situ method of synthesizing graphene molecules (GM) on a TiO<sub>2</sub> surface. This new synthesis method reduced the tendency of graphene molecules to aggregate and paved the way for the integration of GM in optoelectronic and photoelectronic applications. These surface-synthesized GMs have been used in DSSC applications and have achieved a PCE of 0.87% which is the highest recorded efficiency for GM-sensitized solar cells. Jahantigh et al. [171] synthesized nitrogen-doped graphene quantum dots (N-GQD) of average particle size of 9 nm by hydrothermal method and utilized it as a sensitizer for DSSCs together with the N719 dye. With the results from Raman spectra, they were able to identify the high conductivity of N-GQDs and cascaded energy levels between N-GQDs and N719 which facilitate the faster electron transfer from LUMO energy level into the CB of  $TiO_2$ . With these modifications, they were able to achieve a high PCE of 7.49% for their DSSCs. A study by Torres et al. [172] utilized a novel electron donor-acceptor hybrid consisting of NIR absorbing azulenocyanine as an electron donor and few-layer graphene as an electron acceptor. The system was able to absorb a large portion of light from the solar spectrum from UV to near IR region. They were able to introduce this novel hybrid into the DSSC as a photosensitizer and were able to achieve a high PCE of 8.32% under standard conditions.

Yang et al. [173] prepared oxidatively functionalized graphene quantum dots (GQDs) to enhance the light absorption by the photoanode. These GQDs were mixed with N719 dye and utilized to sensitize the DSSC photoanode. Interestingly, they were able to achieve a superior PCE of 8.90% under standard irradiation conditions. Furthermore, lonics

these experimental findings may help to guide the design of GQDs as photosensitizers by tuning their oxidation degree via a facile hydrothermal method. All the aforementioned results testify that the graphene materials could be used as a potential alternative to conventional sensitizers in DSSC photoanodes. Even though the cells containing graphene-based sensitizers only exhibit low PCEs, these cells provide the advantage of large-scale production and commercialization of these devices, which is not possible with expensive and rare metal oxide dye complexes. Most of the studies conclude that the graphene-based sensitizers function by utilizing their quantum effects. The photovoltaic parameters of DSSCs obtained utilizing graphene-based sensitizers are summarized in Table 5.

#### **Graphene-based counter electrodes**

The CE transfers the electrons collected from the external circuit into the electrolyte to catalyze the reduction of the tri-iodide/iodide redox couple for the regeneration of the electrolyte. Platinum-coated conductive ITO or FTO substrates are the most commonly used CE materials. The high electrocatalytic activity of platinum, its high electrochemical stability, and its higher charge transport conductivity make it a prominent material for CE applications. However, due to scarcity, limited supply, and high cost, large-scale and industrial production of DSSCs is hampered [177-179]. .To address these issues, highly abundant, low-cost carbonaceous materials such as graphene and its derivatives have been studied as potential alternatives to platinum [180, 181]. These graphene-based materials have very distinctive features to function as a CE, such as excellent electro-catalytic activity, very high electrical conductivity, high corrosion resistance, and a large specific surface area [125]. However,

**Table 5** The open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (*ff*), and PCE of the DSSCs prepared by using graphene and graphene-based materials as photosensitizers

Photosensitizer	$V_{\rm oc}$ / mV	$J_{\rm sc}$ / mA cm <sup>-2</sup>	ſſ	PCE /%	References
GQDs	370	0.87	0.40	0.13	[174]
N-GQDs	370	1.51	0.43	0.25	[174]
MOF-Graphene	490	1.25	0.43	0.26	[165]
N-GQDs	480	1.49	0.53	0.37	[171]
GO/mangosteen	610	1.00	0.66	0.40	[163]
rGO/TPA-Th-H	530	2.02	0.70	0.80	[175]
Graphene molecules	550	2.50	0.65	0.87	[170]
Gracilaria/GQDs	730	2.26	0.56	0.94	[145]
GQDs	640	3.17	0.62	1.26	[176]
Graphene/MOF	449	20.0	0.44	2.3	[164]
Graphene/N719	830	14.98	0.60	7.47	[172]
N-GQDs/N719	720	17.85	0.59	7.49	[171]
Graphene/azulenocyanine/N719	800	17.01	0.60	8.32	[172]
GQDs/N719	720	19.60	0.66	8.90	[173]

\* MOF - Metal organic frameworks, N-GQDs - Nitrogen-doped graphene quantum dots

the electrocatalytic activity and electrical conductivity of graphene materials are still relatively low compared with Pt, which contributes to poor device performance. In this regard, Choi et al. [182] demonstrated a CE for DSSCs using graphene-based multi-walled carbon nanotubes (GMWC-NTs). The layers of graphene were deposited on a SiO<sub>2</sub>/Si substrate using the drop casting method and achieved a PCE and fill factor of 3.0% and 0.69 respectively. These results suggested that the GMWCNTs are one of the potential candidates for CE in DSSCs.

Zang et al. [183] synthesized graphene nanosheets (GNs) as a substitute for platinum CEs in DSSCs. To investigate the effect of annealing temperature on GN films, the synthesized GNs were screen printed on an FTO substrate and annealed at various temperatures. It was found that the annealing temperature plays a vital role in the graphene nanosheet counter electrode quality, and by optimizing the annealing process of GN films, the DSSC fabricated with GN-based CE annealed at 400°C gained the highest PCE of 6.81% under standard conditions. The study also revealed that the produced result was comparable to a DSSC with a Pt CE, implying that GNs could be used in place of Pt-based CEs. In another interesting study Li et al. [180] fabricated a CE with NiS<sub>2</sub> nanoparticles and NiS<sub>2</sub> nanocomposites together with reduced graphene oxide (NiS<sub>2</sub>@rGO). The fabricated DSSC with NiS<sub>2</sub>@rGO achieved an interesting PCE of 8.55%, which was higher than that of 7.02% for the DSSC with NiS<sub>2</sub> CE, higher than that of 3.14% for the DSSC with rGO CE, and also higher than that of 8.15% for the DSSC with Pt CE. The improved efficiency was attributed to the excellent electrocatalytic performance for redox couple reduction, improved conductivity, and positive synergetic effect of NiS<sub>2</sub> and rGO.

A study was carried out by Wang et al. [184] by reacting Li<sub>2</sub>O and CO at a pressure of 35 psi and 550°C. This reaction was used to synthesize 3D honeycomb-like structured graphene sheets and used them as CE material in DSSCs. They were able to achieve a PCE of 7.8% which was comparable to that of DSSCs with Pt CEs. Another study by Kavan et al. [185] suggested that graphene nanoplatelets (GNP) could outperform the Pt as an electrocatalyst in co-bipyridine (Co(bpy) $_{3}^{3+/2+}$ ) - mediated DSSCs. In this study, GNPs in the form of semi-transparent films on FTO substrates showed high electrocatalytic activity for the  $Co(bpy)_3^{3+/2+}$  redox couple. The final results show that the GNP film is superior to the Pt in both charge transfer resistance and long-term endurance of the cell and was able to achieve a PCE of 9.4% with the GNP CE, which was higher than that of 8.2% with the Pt CE. Ma et al. [186] synthesized SWCNTs/graphene aerogel and used as an alternative to Pt based counter electrodes in DSSCs. Interestingly they were able to achieve a PCE of 8.81% with fabricated CE and 9.64% under assisted by a mirror. The excellent PCE of the cell was attributed to the high electrical conductivity and good electrocatalytic activity from SWCNTs and the large active surface area of 3D structured graphene.

In summary, all these experiments reveal the possibility of using graphene and graphene-based materials as CEs in DSSCs. With extensive research and development, these graphene-based materials could be developed further to enhance their physical and chemical properties for use as a prominent CE material in DSSC applications. Table 6 summarizes the photovoltaic parameters of DSSCs employing graphene-based CEs.

# Conclusions

The study considered the global issues associated with current DSSC technologies and components, such as high production costs, scarcity of materials, and difficulty in largescale applications of DSSC. Motivated by these drawbacks, both academia and industry in recent years have extensively researched various alternative materials that can replace the traditional materials that are used in DSSCs. This article reviewed the uses of one such class of materials, graphene, and its derivatives, with potential applications in various DSSC components, such as transparent electrodes, semiconducting layers, electrolytes, sensitizers, and CEs.

The high optical transparency and high conductivity of graphene can be utilized to fabricate high-performance, transparent conducting electrodes. On the other hand, the high electrocatalytic activity and high electrical conductivity of graphene and graphene-based materials can be utilized to fabricate CEs for DSSCs. Considering the possible enhancement of electron mobility using graphene and reduction of electron-hole charge recombination rate, TiO<sub>2</sub>-graphene hybrid semiconducting films are utilized in DSSCs to improve the PCE of the cell. A large number of studies have proven that graphene and CNTs can be used as additives to current electrolytes, which improves the PCE of the cell. This efficiency enhancement is due to the increase in charge transport in ionic liquids and the use of carbon materials as a catalyst for the electrochemical reduction of the redox couple. Another series of studies has shown the ability to use graphene as a sensitizer in DSSCs, which use the quantum mechanical effects of graphene materials.

These graphene-based DSSCs show some improvements in their performance, but still less stable and inefficient for industrial applications. Therefore, more research is needed to optimize the optoelectronic properties, long-term stability, and power conversion efficiencies of dye-sensitized solar cells in the future. However, recent trends (Fig. 2) indicated that the researcher's interests are fading mainly due to marginal improvements and challenges associated with DSSCs. **Table 6** The open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (*ff*), and PCE of the DSSCs prepared by using graphene and graphene-based materials as counter electrodes

CE configuration	$V_{\rm oc}$ / mV	$J_{\rm sc}$ / mA cm <sup>-2</sup>	ff	PCE /%	References
Graphene nanosheets	770	3.6	0.39	1.0	[187]
Graphene paper	600	13.87	0.18	1.50	[188]
GMWNTs	760	5.6	0.70	3.0	[182]
rGO nanoribbons	729	14.17	0.32	3.31	[189]
rGO	690	9.89	0.59	4.04	[190]
N-rGO	650	12.06	0.54	4.26	[191]
PANI-rGO	790	11.50	0.59	5.47	[192]
Graphene	700	13.1	0.64	5.87	[193]
GNs	747	16.99	0.53	6.81	[183]
MWCNT/rGO	700	16.87	0.59	6.91	[194]
rGO/Mn	740	17.20	0.58	7.47	[195]
MWCNT/graphene composite	750	16.05	0.62	7.55	[196]
HSG	773	27.2	0.37	7.80	[184]
Graphite / SnO <sub>2</sub>	731	18.5	0.59	7.95	[197]
Co <sub>3</sub> S <sub>4</sub> /rGO	760	15.70	0.68	8.08	[198]
NiS <sub>2</sub> /rGO	749	16.55	0.69	8.55	[180]
RGO/SnO <sub>2</sub> /PANI	728	19.2	0.62	8.68	[199]
GNP	878	14.8	0.72	9.40	[185]
SWCNT/graphene aerogels	740	22.90	56.4	9.64	[186]

\* N-rGO - Nitrogen-doped reduced graphene oxide

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#### Declarations

Competing interests The authors declare no competing interests.

# References

- 1. Bradford T (2008) Solar revolution: the economic transformation of the global energy industry. MIT Press
- Bella F (2015) Polymer electrolytes and perovskites: lights and shadows in photovoltaic devices. Electrochim Acta 175:151–161
- Güney T (2019) Renewable energy, non-renewable energy and sustainable development. Int J Sustain Dev World Ecol 26(5):389–397

- 4. Ali S, Anwar S, Nasreen S (2017) Renewable and Non-Renewable Energy and its Impact on Environmental Quality in South Asian Countries. Forman J Econ Stud 13
- Tugcu CT, Ozturk I, Aslan A (2012) Renewable and non-renewable energy consumption and economic growth relationship revisited: evidence from G7 countries. Energy Econ 34(6):1942–1950
- Nazeeruddin MK, Baranoff E, Grätzel M (2011) Dye-sensitized solar cells: A brief overview. Sol Energy 85(6):1172–1178
- National Renewable Energy Laboratory, Best Research-Cell Efficiency Chart. Available from: https://www.nrel.gov/pv/cell-effic iency.html (Accessed 17, May 2024)
- Kakiage K, Aoyama Y, Yano T, Oya K, Fujisawa JI, Hanaya M (2015) Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. Chem Commun 51(88):15894–15897
- Ren Y, Zhang D, Suo J, Cao Y, Eickemeyer FT, Vlachopoulos N, Zakeeruddin SM, Hagfeldt A, Grätzel M (2023) Hydroxamic acid pre-adsorption raises the efficiency of cosensitized solar cells. Nature 613(7942):60–65
- West W (1974) Proceedings of vogel centennial symposium. Photogr Sci Eng 18:35
- Tsubomura H, Matsumura M, Nomura Y, Amamiya T (1976) Dye Sensitized Zinc Oxide: Aqueous Electrolyte Platinum Photocell. Nature 261:402–403
- Desilvestro J, Graetzel M, Kavan L, Moser J, Augustynski J (1985) Highly efficient sensitization of titanium dioxide. J Am Chem Soc 107(10):2988–2990.138
- O'Regan B, Gratzel M (1991) A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature 353:737–740
- Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Müller E, Liska P, Vlachopoulos N, Grätzel M (1993) Conversion of light to electricity by cis-X2bis (2, 2'-bipyridyl-4, 4'-dicarboxylate) ruthenium (II) charge-transfer sensitizers (X= Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes. J Am Chem Soc 115(14):6382–6390

- Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han L (2006) Dye-sensitized solar cells with conversion efficiency of 11.1%. Jpn J Appl Phys 45(7L):L638
- Kakiage K, Aoyama Y, Yano T, Otsuka T, Kyomen T, Unno M, Hanaya M (2014) An achievement of over 12 percent efficiency in an organic dye-sensitized solar cell. Chem Commun 50(48):6379–6381
- Arka GN, Prasad SB, Singh S (2022) Transparent Conductive Oxide Nanolayers for Dye-sensitized Solar Cell. In: Nanomaterials for Advanced Technologies. Springer Nature Singapore, Singapore, pp 35–48
- Sima C, Grigoriu C, Antohe S (2010) Comparison of the dyesensitized solar cells performances based on transparent conductive ITO and FTO. Thin Solid Films 519(2):595–597
- Jose R, Thavasi V, Ramakrishna S (2009) Metal oxides for dye-sensitized solar cells. J Am Ceram Soc 92(2):289–301
- Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L, Luo G (2015) Electrolytes in dye-sensitized solar cells. Chem Rev 115(5):2136–2173
- 21. Wu J, Lan Z, Hao S, Li P, Lin J, Huang M et al (2008) Progress on the electrolytes for dye-sensitized solar cells. Pure Appl Chem 80(11):2241–2258
- Wang M, Grätzel C, Zakeeruddin SM, Grätzel M (2012) Recent developments in redox electrolytes for dye-sensitized solar cells. Energy Environ Sci 5(11):9394–9405
- Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L et al (2017) Counter electrodes in dye-sensitized solar cells. Chem Soc Rev 46(19):5975–6023
- Huang Z, Liu X, Li K, Li D, Luo Y, Li H et al (2007) Application of carbon materials as counter electrodes of dye-sensitized solar cells. Electrochem Commun 9(4):596–598
- 25. Ma T, Fang X, Akiyama M, Inoue K, Noma H, Abe E (2004) Properties of several types of novel counter electrodes for dyesensitized solar cells. J Electroanal Chem 574(1):77–83
- Ranabhat K, Chernyshova KF, Revina AA, Lapshinsky VA, Patrikeev LN (2020) Development of high-efficient dye-sensitized solar cells using nanoparticles. 1(2):115–122
- Mehmood U, Rahman SU, Harrabi K, Hussein IA, Reddy BVS (2014) Recent advances in dye sensitized solar cells. Adv Mater Sci Eng 2014
- Andualem A, Demiss S (2018) Review on Dye-Sensitized Solar Cells (DSSCs). Edelweiss Appl Sci Technol 2(1):145–150
- Wang YQ, Wei ZD, Cai HY, Zhang Q, Zhao QL (2010) Pt/ FTO Counter Electrode for Dye-Sensitized Solar Cells Prepared by Sputtering-Displacement. Acta Phys Chim Sin 26(11):2957–2961
- Kawashima T, Ezure T, Okada K, Matsui H, Goto K, Tanabe N (2004) FTO/ITO double-layered transparent conductive oxide for dye-sensitized solar cells. J Photochem Photobiol A Chem 164(1-3):199–202
- Chalker PR, Marshall PA, Romani S, Roberts JW, Irvine SJ, Lamb DA, Clayton AJ, Williams PA (2013) Atomic layer deposition of Ga-doped ZnO transparent conducting oxide substrates for CdTe-based photovoltaics. J Vac Sci Technol A 31(1):01A120
- 32. Kozhukharov S, Tchaoushev S (2013) Spray pyrolysis equipment for various applications. J Chem Technol Metall 48(1):111–118
- Rozati SM, Ganj T (2004) Transparent conductive Sn-doped indium oxide thin films deposited by spray pyrolysis technique. Renew Energy 29(10):1671–1676
- Bandara TMWJ, Aththanayake AAAP, Kumara GRA, Samarasekara P, DeSilva LA, Tennakone K (2021) Transparent and conductive F-Doped SnO2 nanostructured thin films by sequential nebulizer spray pyrolysis. MRS Adv 6:417–421
- 35. Tatar D, Turgut G, Düzgün B (2013) Effect of substrate temperature on the crystal growth orientation and some physical

properties of SnO2: F thin films deposited by spray pyrolysis technique. Rom J Phys 58(1-2):143–158

- 36. Umar AA, Nafisah S, Saad SKM, Tan ST, Balouch A, Salleh MM, Oyama M (2014) Poriferous microtablet of anatase TiO2 growth on an ITO surface for high-efficiency dye-sensitized solar cells. Sol Energy Mater Sol Cells 122:174–182
- 37. Nishshanke GBMMM, Thilakarathna BDKK, Albinsson I, Mellander BE, Bandara TMWJ (2021) Multi-layers of TiO2 nanoparticles in the photoelectrode and binary iodides in the gel polymer electrolyte based on poly (ethylene oxide) to improve quasi solid-state dye-sensitized solar cells. J Solid State Electrochem 25:707–720
- Sengupta D, Das P, Mondal B, Mukherjee K (2016) Effects of doping, morphology and film-thickness of photo-anode materials for dye sensitized solar cell application–A review. Renew Sustain Energy Rev 60:356–376
- 39. Bandara TMWJ, DeSilva LA, Ratnasekera JL, Hettiarachchi KH, Wijerathna AP, Thakurdesai M et al (2019) High efficiency dyesensitized solar cell based on a novel gel polymer electrolyte containing RbI and tetrahexylammonium iodide (Hex4NI) salts and multi-layered photoelectrodes of TiO2 nanoparticles. Renew Sustain Energy Rev 103:282–290
- 40. Dissanayake MAKL, Thotawatthage CA, Senadeera GKR, Bandara TMWJ, Jayasundera WJMJSR, Mellander BE (2012) Efficiency enhancement by mixed cation effect in dye-sensitized solar cells with PAN based gel polymer electrolyte. J Photochem Photobiol A Chem 246:29–35
- Bandara TMWJ, Dissanayake MAKL, Albinsson I, Mellander BE (2010) Dye-sensitized, nano-porous TiO2 solar cell with poly (acrylonitrile): MgI2 plasticized electrolyte. J Power Sources 195(11):3730–3734
- 42. Bandara TMWJ, Jayasundara WJMJSR, Fernado HDNS, Dissanayake MAKL, De Silva LAA, Albinsson, Mellander BE (2015) Efficiency of 10% for quasi-solid state dye-sensitized solar cells under low light irradiance. J Appl Electrochem 45:289–298
- Marinado T (2009) Photoelectrochemical studies of dye-sensitizedsolar cells using organic dyes. Ph.D. Thesis, KTH Royal Institute of Technology, Sweden
- 44. Flores IC, de Freitas JN, Longo C, De Paoli MA, Winnischofer H, Nogueira AF (2007) Dye-sensitized solar cells based on TiO2 nanotubes and a solid-state electrolyte. J Photochem Photobiol A Chem 189(2-3):153–160
- Cavallo C, Di Pascasio F, Latini A, Bonomo M, Dini D (2017) Nanostructured semiconductor materials for dye-sensitized solar cells. J Nanomater 2017
- 46. Lin LY, Yeh MH, Lee CP, Chou CY, Vittal R, Ho KC (2012) Enhanced performance of a flexible dye-sensitized solar cell with a composite semiconductor film of ZnO nanorods and ZnO nanoparticles. Electrochim Acta 62:341–347
- Baxter JB, Aydil ES (2006) Dye-sensitized solar cells based on semiconductor morphologies with ZnO nanowires. Sol Energy Mater Sol Cells 90(5):607–622
- Chappel S, Zaban A (2002) Nanoporous SnO2 electrodes for dye-sensitized solar cells: improved cell performance by the synthesis of 18 nm SnO2 colloids. Sol Energy Mater Sol Cells 71(2):141–152
- 49. Cho TY, Ko KW, Yoon SG, Sekhon SS, Kang MG, Hong YS, Han CH (2013) Efficiency enhancement of flexible dye-sensitized solar cell with sol-gel formed Nb2O5 blocking layer. Curr Appl Phys 13(7):1391–1396
- Pazoki M, Taghavinia N, Hagfeldt A, Boschloo G (2014) Mesoporous TiO2 microbead electrodes for cobalt-mediator-based dye-sensitized solar cells. J Phys Chem C 118(30):16472–16478
- 51. Gonzalez-Valls I, Yu Y, Ballesteros B, Oro J, Lira-Cantu M (2011) Synthesis conditions, light intensity and temperature

effect on the performance of ZnO nanorods-based dye sensitized solar cells. J Power Sources 196(15):6609–6621

- 52. Yildiz ZK, Atilgan A, Atli A, Özel K, Altinkaya C, Yildiz A (2019) Enhancement of efficiency of natural and organic dye sensitized solar cells using thin film TiO2 photoanodes fabricated by spin-coating. J Photochem Photobiol A Chem 368:23–29
- Pichot F, Pitts JR, Gregg BA (2000) Low-temperature sintering of TiO2 colloids: application to flexible dye-sensitized solar cells. Langmuir 16(13):5626–5630
- DeSilva LA, Thakurdesai M, Bandara TMWJ, Preston J, Johnson W, Gaquere-Parker A, Survase S (2018) Synthesis of dense TiO2 nanoparticle multilayers using spin coating technique. Appl Phys A 124:1–7
- Schmidt-Mende L, Gratzel M (2006) TiO2 pore-filling and its effect on the efficiency of solid-state dye-sensitized solar cells. Thin Solid Films 500(1-2):296–301
- Liu G, Wang X, Wang L, Chen Z, Li F, Lu GQM, Cheng HM (2009) Drastically enhanced photocatalytic activity in nitrogen doped mesoporous TiO2 with abundant surface states. J Colloid Interface Sci 334(2):171–175
- Ito S, Chen P, Comte P, Nazeeruddin MK, Liska P, Pechy P, Gratzel M (2007) Fabrication of screen-printing pastes from TiO2 powders for dye-sensitised solar cells. Prog Photovolt Res Appl 15(7):603–612
- Toma FL, Bertrand G, Klein D, Meunier C, Begin S (2008) Development of photocatalytic active TiO2 surfaces by thermal spraying of nanopowders. J Nanomater 2008
- Okuya M, Nakade K, Osa D, Nakano T, Kumara GRA, Kaneko S (2004) Fabrication of dye-sensitized solar cells by spray pyrolysis deposition (SPD) technique. J Photochem Photobiol A Chem 164(1-3):167–172
- Bella F, Verna A, Gerbaldi C (2018) Patterning dye-sensitized solar cell photoanodes through a polymeric approach. A perspective. Mater Sci Semicond Process 73:92–98. https://doi.org/10. 1016/j.mssp.2017.07.030
- Friedrich D (2011) A study of charge transfer kinetics in dyesensitized surface conductivity solar cells, Ph.D. https://doi.org/ 10.5442/D0007 [Accessed 26 February 2020]
- Amano F, Yamamoto A, Kumagai J (2022) Highly Active Rutile TiO2 for Photocatalysis under Violet Light Irradiation at 405 nm. Catalysts 12(10):1079
- Morgunov V, Lytovchenko S, Chyshkala V, Riabchykov D, Matviienko D (2021) Comparison of Anatase and Rutile for Photocatalytic Application: the Short Review. East Eur J Phys 4:18–30
- 64. Kay A, Grätzel M (1996) Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. Sol Energy Mater Sol Cells 44(1):99–117
- Narayan MR (2012) Dye sensitized solar cells based on natural photosensitizers. Renew Sustain Energy Rev 16(1):208–215
- Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H (2010) Dye-sensitized solar cells. Chem Rev 110(11):6595–6663
- 67. Ooyama Y, Harima Y (2012) Photophysical and electrochemical properties, and molecular structures of organic dyes for dyesensitized solar cells. ChemPhysChem 13(18):4032–4080
- Islam A, Sugihara H, Hara K, Singh LP, Katoh R, Yanagida M, Takahashi Y, Murata S, Arakawa H (2001) Sensitization of nanocrystalline TiO2 film by ruthenium (II) diiminedithiolate complexes. J Photochem Photobiol A Chem 145(1-2):135–141
- Klein C, Nazeeruddin MK, Di Censo D, Liska P, Gratzel M (2004) Amphiphilicruthenium sensitizers and their applications in dye-sensitized solar cells. Inorg Chem 43(14):4216–4226
- Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK et al (2011) Porphyrin-sensitized solar cells with cobalt (II/ III)–based redox electrolyte exceed 12 percent efficiency. Science 334(6056):629–634

- Kuciauskas D, Freund MS, Gray HB, Winkler JR, Lewis NS (2001) Electron transfer dynamics in nanocrystalline titanium dioxide solar cells sensitized with ruthenium or osmium polypyridyl complexes. J Phys Chem B 105(2):392–403
- 72. Geary EA, Yellowlees LJ, Jack LA, Oswald ID, Parsons S, Hirata N, Durrant JR, Robertson N (2005) Synthesis, structure, and properties of [Pt(II)(diimine)(dithiolate)] dyes with 3, 3 '-, 4, 4 '-, and 5, 5 '-disubstitutedbipyridyl: applications in dyesensitized solar cells. Inorg Chem 44(2):242–250
- 73. Alonso-Vante N, Nierengarten JF, Sauvage JP (1994) Spectral sensitization of large-band-gap semiconductors (thin films and ceramics) by a carboxylatedbis (1, 10-phenanthroline) copper (I) complex. J Chem Soc Dalton Trans (11):1649–1654
- 74. Ferrere S, Gregg BA (1998) Photosensitization of TiO2 by [FeII (2, 2 '-bipyridine-4, 4 '-dicarboxylic acid)2(CN)2]: band selective electron injection from ultra-short-lived excited states. J Am Chem Soc 120(4):843–844
- Ito S, Miura H, Uchida S, Takata M, Sumioka K, Liska P, Comte P, Pechy P, Grätzel M (2008) High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline dye. Chem Commun 41:5194–5196
- Horiuchi T, Miura H, Uchida S (2003) Highly-efficient metalfree organic dyes for dye-sensitized solar cells. Chem Commun 24:3036–3037
- 77. Hara K, Wang ZS, Sato T, Furube A, Katoh R, Sugihara H, Dan-oh Y, Kasada C, Shinpo A, Suga S (2005) Oligothiophenecontaining coumarin dyes for efficient dye-sensitized solar cells. J Phys Chem B 109(32):15476–15482
- Wang ZS, Koumura N, Cui Y, Takahashi M, Sekiguchi H, Mori A, Kubo T, Furube A, Hara K (2008) Hexylthiophene-functionalized carbazole dyes for efficient molecular photovoltaics: tuning of solar-cell performance by structural modification. Chem Mater 20(12):3993–4003
- Chen R, Yang X, Tian H, Sun L (2007) Tetrahydroquinoline dyes with different spacers for organic dye-sensitized solar cells. J Photochem Photobiol A Chem 189(2-3):295–300
- Sen A, Putra MH, Biswas AK, Behera AK, Groβ A (2023) Insight on the choice of sensitizers/dyes for dye sensitized solar cells: A review. Dyes Pigments:111087
- Bella F, Sacco A, Massaglia G et al (2015) Dispelling clichés at the nanoscale: the true effect of polymer electrolytes on the performance of dye-sensitized solar cells. Nanoscale 7:12010–12017
- Bella F, Fagiolari L, Bonomo M, Galliano S, Viscardi G, Barolo C (2021) Water-based solar cells: electrochemical behavior of state-of-art electrodes and electrolytes. In: Titolo volume non avvalorato. International Society of Electrochemistry, p 1
- 83. Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod BF, Ashari-Astani N, Grätzel M (2014) Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. Nat Chem 6(3):242–247
- Nishshanke GBMMM, Arof AK, Bandara TMWJ (2020) Review on mixed cation effect in gel polymer electrolytes for quasi solidstate dye-sensitized solar cells. Ionics 26:3685–3704
- Rondán-Gómez V, Montoya De Los Santos I, Seuret-Jiménez D, Ayala-Mató F, Zamudio-Lara A, Robles-Bonilla T, Courel M (2019) Recent advances in dye-sensitized solar cells. Appl Phys A 125:1–24
- Chen JH, Jang C, Xiao S, Ishigami M, Fuhrer MS (2008) Intrinsic and extrinsic performance limits of graphene devices on SiO2. Nat Nanotech 3:206
- 87. Geim AK, Kim P (2008) Carbon wonderland. Sci Am 298:90
- Novoselov KS, Geim AK, Morozov SV, Jiang DE, Zhang Y, Dubonos SV et al (2004) Electric field effect in atomically thin carbon films. Science 306(5696):666–669
- https://www.nobelprize.org/prizes/physics/2010/summary/ (Accessed 08 February 2023)

- Kuzmenko AB, Heumen EV, Carbone F, Marel DVD (2008) Universal optical conductance of graphite. Phys Rev Lett 100:117401
- 91. Geim AK, Novoselov KS (2007) The rise of graphene. Nat Mater 6(183)
- 92. https://www.compositesworld.com/articles/graphene-101-formsproperties-and-applications (Accessed 08 February 2023)
- Tiwari SK, Sahoo S, Wang N, Huczko A (2020) Graphene research and their outputs: Status and prospect. J Sci Adv Mater Devices 5(1):10–29
- 94. Bandara TMWJ, Thennakoon TMAAB, Nishshanke GBMMM (2023) Preparation, characterization, and applications of graphene-based quantum dots (GQDs). In: Functional Materials from Carbon, Inorganic, and Organic Sources. Woodhead Publishing, pp 21–69
- Cooper DR, D'Anjou B, Ghattamaneni N, Harack B, Hilke M, Horth A, Yu V (2012) Experimental review of graphene. Int Sch Res Not 2012
- 96. Lee XJ, Hiew BYZ, Lai KC, Lee LY, Gan S, Thangalazhy-Gopakumar S, Rigby S (2019) Review on graphene and its derivatives: Synthesis methods and potential industrial implementation. J Taiwan Inst Chem Eng 98:163–180
- Zhong YL, Tian Z, Simon GP, Li D (2015) Scalable production of graphene via wet chemistry: progress and challenges. Mater Today 18(2):73–78
- Yu H, Zhang B, Bulin C, Li R, Xing R (2016) High-efficient synthesis of graphene ox- ide based on improved hummers method. Sci Rep 6:36143
- Edwards RS, Coleman KS (2013) Graphene synthesis: relationship to applications. Nanoscale 5(1):38–51
- Ambrosi A, Chua CK, Bonanni A, Pumera M (2014) Electrochemistry of graphene and related materials. Chem Rev 114:7150–7188
- 101. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Electric field effect in atomically thin carbon films. Science 306(5696):666–669
- 102. Wu X, Liu Y, Yang H, Shi Z (2016) Large-scale synthesis of high-quality graphene sheets by an improved alternating current arc-discharge method. RSC Adv 6:93119–93124
- 103. Güler Ö, Güler SH, Selen V, Albayrak MG, Evin E (2016) Productionofgraphene layer by liquid-phase exfoliation with low sonication power and sonication time from synthesized expanded graphite. Fullerenes Nanotubes Carbon Nanostruct 24:123–127
- 104. Haar S, Bruna M, Lian JX, Tomarchio F, Olivier Y, Mazzaro R et al (2016) Liq- uid-phase exfoliation of graphite into singleand few-layer graphene with  $\alpha$ -functionalized alkanes. J Phys Chem Lett 7:2714–2721
- 105. Jacobberger RM, Machhi R, Wroblewski J, Taylor B, Gillian-Daniel AL, Arnold MS (2015) Simple graphene synthesis via chemical vapor deposition. J Chem Educ 92:1903–1907
- Son M, Ham M-H (2017) Low-temperature synthesis of graphene by chemical vapor deposition and its applications. FlatChem 5:40–49
- Huang H, Chen S, Wee ATS, Chen W (2014) 1 Epitaxial growth of graphene on silicon carbide (SiC). Graphene: Woodhead Publishing, pp 3–26
- 108. Yazdi G, Iakimov T, Yakimova R et al (2016) Crystal 6:53
- 109. Yang Y, Liu R, Wu J, Jiang X, Cao P, Hu X, Pan T, Qiu C, Yang J, Song Y, Wu D, Su Y et al (2015) Sci Rep 5:13480
- 110. Singh V, Joung D, Zhai L, Das S, Khondaker SI, Seal S et al (2011) Prog Mater Sci 56:1178–1271
- 111. Geim AK (2009) Graphene: status and prospects. Science 324(5934):1530–1534

- Novoselov KS, Geim AK, Morozov SV et al (2005) Twodimensional gas of massless Dirac fermions in graphene. Nature 438(7065):197–200
- Emtsev KV, Bostwick A, Horn K et al (2009) Towards wafersize graphene layers by atmospheric pressure graphitization of silicon carbide. Nat Mater 8(3):203–207
- Kim KS, Zhao Y, Jang H et al (2009) Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature 457(7230):706–710
- Bae S, Kim H, Lee Y et al (2010) Roll-to-roll production of 30-inch graphene films for transparent electrodes. Nat Nanotechnol 5(8):574–578
- 116. Li X, Magnuson CW, Venugopal A et al (2010) Graphene films with large domain size by a two-step chemical vapor deposition process. Nano Lett 10(11):4328–4334
- 117. Glöser S, Espinoza LT, Gandenberger C, Faulstich M (2015) Raw material criticality in the context of classical risk assessment. Resour Policy 44:35–46
- 118. Li X, Zhu Y, Cai W, Borysiak M, Han B, Chen D, Piner RD, Colombo L, Ruoff RS (2009) Transfer of large-area graphene films for high-performance transparent conductive electrodes. Nano Lett 9:4359–4363
- 119. Bae, S., Kim, H. K., Lee, Y., Xu, X., Park, J. S., Zheng, Y.,... & Iijima, S. (2009). 30 inch roll-based production of high-quality graphene films for flexible transparent electrodes. arXiv preprint arXiv:0912.5485.
- Bonaccorso F, Sun Z, Hasan T, Ferrari AC (2010) Graphene photonics and optoelectronics. Nat Photonics 4(9):611–622
- Wang X, Zhi L, Müllen K (2008) Transparent, conductive graphene electrodes for dye-sensitized solar cells. Nano Lett 8(1):323–327
- 122. Selopal GS, Milan R, Ortolani L, Morandi V, Rizzoli R, Sberveglieri G et al (2015) Graphene as transparent front contact for dye sensitized solar cells. Sol Energy Mater Sol Cells 135:99–105
- 123. Roh KM, Jo EH, Chang H, Han TH, Jang HD (2015) High performance dye-sensitized solar cells using graphene modified fluorine-doped tin oxide glass by Langmuir–Blodgett technique. J Solid State Chem 224:71–75
- 124. Dong P, Zhu Y, Zhang J, Peng C, Yan Z, Li L et al (2014) Graphene on metal grids as the transparent conductive material for dye sensitized solar cell. J Phys Chem C 118(45):25863–25868
- Muchuweni E, Martincigh BS, Nyamori VO (2020) Recent advances in graphene-based materials for dye-sensitized solar cell fabrication. RSC Adv 10(72):44453–44469
- 126. Shahid MU, Mohamed NM, Khatani M, Muhsan AS, Samsudin A, Irshad MI, Zaine SNA (2017) Graphene modified FTO/TiO2 interface photoelectrode for improved performance of dye sensitized solar cells. AIP Conf Proc 1901(1):020004 AIP Publishing LLC
- 127. Song M, Seo HK, Ameen S, Akhtar MS, Shin HS (2014) Low resistance transparent graphene-like carbon thin film substrates for high performance dye sensitized solar cells. Electrochim Acta 115:559–565
- Bhaviripudi S, Jia X, Dresselhaus MS, Kong J (2010) Role of kinetic factors in chemical vapor deposition synthesis of uniform large area graphene using copper catalyst. Nano Lett 10(10):4128–4133
- 129. Fang X, Li M, Guo K, Zhu Y, Hu Z, Liu X et al (2012) Improved properties of dye-sensitized solar cells by incorporation of graphene into the photoelectrodes. Electrochim Acta 65:174–178
- 130. Basu K, Selopal GS, Mohammadnezad M, Akilimali R, Wang ZM, Zhao H et al (2020) Hybrid graphene/metal oxide anodes for efficient and stable dye sensitized solar cell. Electrochim Acta 349:136409

- 131. Yang N, Zhai J, Wang D, Chen Y, Jiang L (2010) Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells. ACS Nano 4(2):887–894
- 132. Chen T, Hu W, Song J, Guai GH, Li CM (2012) Interface functionalization of photoelectrodes with graphene for high performance dye-sensitized solar cells. Adv Funct Mater 22(24):5245–5250
- 133. Fang X, Li M, Guo K, Li J, Pan M, Bai L et al (2014) Graphene quantum dots optimization of dye-sensitized solar cells. Electrochim Acta 137:634–638
- Fan J, Liu S, Yu J (2012) Enhanced photovoltaic performance of dye-sensitized solar cells based on TiO 2 nanosheets/graphene composite films. J Mater Chem 22(33):17027–17036
- 135. Wang C, Zhu Y, Ge Z, Shi R, Chen T, Chen Z, Liu J (2020) The feasible photoanode of graphene oxide/zinc aluminum mixed metal oxides for the dye-sensitized solar cell. Colloid Interface Sci Commun 39:100313
- Le TTN, Le VC (2020) Synthesis of zinc oxide/reduced graphene oxide composites for fabrication of anodes in dye-sensitized solar cells. Chem Eng 78
- 137. Nien YH, Chen HH, Hsu HH, Kuo PY, Chou JC, Lai CH et al (2019) Enhanced photovoltaic conversion efficiency in dye-sensitized solar cells based on photoanode consisting of TiO2/GO/ Ag nanofibers. Vacuum 167:47–53
- Gao N, Wan T, Xu Z, Ma L, Ramakrishna S, Liu Y (2020) Nitrogen doped TiO2/Graphene nanofibers as DSSCs photoanode. Mater Chem Phys 255:123542
- 139. Javed HMA, Qureshi AA, Mustafa MS, Que W, Mahr MS, Shaheen A et al (2019) Advanced Ag/rGO/TiO2 ternary nanocomposite based photoanode approaches to highly-efficient plasmonic dye-sensitized solar cells. Opt Commun 453:124408
- 140. Low FW, Lai CW, Abd Hamid SB (2017) Study of reduced graphene oxide film incorporated of TiO 2 species for efficient visible light driven dye-sensitized solar cell. J Mater Sci Mater Electron 28:3819–3836
- 141. Low FW, Lai CW, Abd Hamid SB (2017) Surface modification of reduced graphene oxide film by Ti ion implantation technique for high dye-sensitized solar cells performance. Ceram Int 43(1):625–633
- 142. Krishnamoorthy D, Prakasam A (2020) Preparation of MoS2/ graphene nanocomposite-based photoanode for dye-sensitized solar cells (DSSCs). Inorg Chem Commun 118:108016
- 143. Pattarith K, Areerob Y (2020) Fabrication of Ag nanoparticles adhered on RGO based on both electrodes in dye-sensitized solar cells (DSSCs). Renewables Wind Water Solar 7(1):1–10
- 144. Tang B, Yu H, Peng H, Wang Z, Li S, Ma T, Huang W (2018) Graphene based photoanode for DSSCs with high performances. RSC Adv 8(51):29220–29227
- 145. Krishnamoorthy D, Prakasam A (2020) Low-cost and novel preparation of porous NiS2/graphene heterojunctions photoanodes for high-efficiency dye-sensitized solar cells. Inorg Chem Commun 119:108063
- 146. Marchezi PE, Sonai GG, Hirata MK, Schiavon MA, Nogueira AF (2016) Understanding the role of reduced graphene oxide in the electrolyte of dye-sensitized solar cells. J Phys Chem C 120(41):23368–23376
- 147. Roy-Mayhew JD, Aksay IA (2014) Graphene materials and their use in dye-sensitized solar cells. Chem Rev 114(12):6323–6348
- 148. Ahmad I, Khan U, Gun'ko YK (2011) Graphene, carbon nanotube and ionic liquid mixtures: towards new quasi-solid state electrolytes for dye sensitised solar cells. J Mater Chem 21(42):16990–16996
- 149. Lin B, Feng T, Chu F, Zhang S, Yuan N, Qiao G, Ding J (2015) Poly (ionic liquid)/ionic liquid/graphene oxide composite quasi solid-state electrolytes for dye sensitized solar cells. RSC Adv 5(70):57216–57222

- 150. Byrne O, Ahmad I, Surolia PK, Gun'ko YK, Thampi KR (2014) The optimisation of dye sensitised solar cell working electrodes for graphene and SWCNTs containing quasi-solid state electrolytes. Sol Energy 110:239–246
- 151. Khannam M, Boruah R, Dolui SK (2017) An efficient quasisolid state dye sensitized solar cells based on graphene oxide/ gelatin gel electrolyte with NiO supported TiO2 photoanode. J Photochem Photobiol A Chem 335:248–258
- 152. Kowsari E, Chirani MR (2017) High efficiency dye-sensitized solar cells with tetra alkyl ammonium cation-based ionic liquid functionalized graphene oxide as a novel additive in nanocomposite electrolyte. Carbon 118:384–392
- 153. Venkatesan S, Darlim ES, Tsai M-H, Teng H, Lee Y-L (2018) ACS Appl Mater Interfaces 10:10955–10964
- 154. Zheng J (2017) Graphene tailored polymer gel electrolytes for 9.1%-efficiency quasi-solid-state dye-sensitized solar cells. J Power Sources 348:239–245
- 155. Brennan LJ, Barwich ST, Satti A, Faure A, Gun'ko YK (2013) Graphene-ionic liquid electrolytes for dye sensitised solar cells. J Mater Chem A 1(29):8379–8384
- 156. Porfarzollah A, Mohammad-Rezaei R, Bagheri M (2020) Ionic liquid-functionalized graphene quantum dots as an efficient quasi-solid-state electrolyte for dye-sensitized solar cells. J Mater Sci Mater Electron 31:2288–2297
- 157. Shrivatsav R, Mahalingam V, Narayanan EL, Balaji NN, Balu M, Prasad RK, Kumaresan D (2018) Characterization of poly methyl methaacrylate and reduced graphene oxide composite for application as electrolyte in dye sensitized solar cells. Mater Res Express 5(4):046204
- 158. Manafi P, Nazockdast H, Karimi M, Sadighi M, Magagnin L (2020) Microstructural development and rheological study of a nanocomposite gel polymer electrolyte based on functionalized graphene for dye-sensitized solar cells. Polymers 12(7):1443
- 159. Velten JA, Carretero-González J, Castillo-Martínez E, Bykova J, Cook A, Baughman R, Zakhidov A (2011) Photoinduced optical transparency in dye-sensitized solar cells containing graphene nanoribbons. J Phys Chem C 115(50):25125–25131
- 160. Yuan S, Tang Q, He B, Zhao Y (2014) Multifunctional graphene incorporated conducting gel electrolytes in enhancing photovoltaic performances of quasi-solid-state dye-sensitized solar cells. J Power Sources 260:225–232
- 161. Yuan S, Tang Q, Hu B, Ma C, Duan J, He B (2014) Efficient quasi-solid-state dye-sensitized solar cells from graphene incorporated conducting gel electrolytes. J Mater Chem A 2(8):2814–2821
- 162. Mishra A, Fischer MK, Bäuerle P (2009) Metal-free organic dyes for dye-sensitized solar cells: From structure: Property relationships to design rules. Angew Chem Int Ed 48(14):2474–2499
- 163. Ismail M, Ludin NA, Hamid NH, Ibrahim MA, Zulfakar MS, Mohamed NM, Sopian K (2017) Characterizations of natural dye from Garcinia mangostana with graphene oxide (GO) as sensitizer in dye-sensitizer solar cells. AIP Conf Proc 1838(1):020017 AIP Publishing LLC
- 164. Kaur R, Kim KH, Deep A (2017) A convenient electrolytic assembly of graphene-MOF composite thin film and its photoanodic application. Appl Surf Sci 396:1303–1309
- 165. Lee DY, Shinde DV, Yoon SJ, Cho KN, Lee W, Shrestha NK, Han SH (2014) Cu-based metal–organic frameworks for photovoltaic application. J Phys Chem C 118(30):16328–16334
- Williams KJ, Nelson CA, Yan X, Li LS, Zhu X (2013) Hot electron injection from graphene quantum dots to TiO2. ACS Nano 7(2):1388–1394
- 167. Tielrooij KJ, Song JCW, Jensen SA, Centeno A, Pesquera A, Zurutuza Elorza A, Bonn M, Levitov LS, Koppens FHL (2013) Nat Phys 9:248

- Yan X, Cui X, Li B, Li LS (2010) Large, solution-processable graphene quantum dots as light absorbers for photovoltaics. Nano Lett 10(5):1869–1873
- 169. Yan X, Li B, Cui X, Wei Q, Tajima K, Li LS (2011) Independent tuning of the band gap and redox potential of graphene quantum dots. J Phys Chem Lett 2(10):1119–1124
- 170. Ji Z, Wu R, Adamska L, Velizhanin KA, Doorn SK, Sykora M (2014) In situ synthesis of graphene molecules on TiO2: Application in sensitized solar cells. ACS Appl Mater Interfaces 6(22):20473–20478
- 171. Jahantigh F, Ghorashi SMB, Mozaffari S (2020) Orange photoluminescent N-doped graphene quantum dots as an effective cosensitizer for dye-sensitized solar cells. J Solid State Electrochem 24:883–889
- 172. Volland M, Lennert A, Roth A, Ince M, Torres T, Guldi DM (2019) Azulenocyanines immobilized on graphene; on the way to panchromatic absorption and efficient DSSC blocking layers. Nanoscale 11(22):10709–10715
- Yang W, Park IW, Lee JM, Choi H (2020) Influence of Oxidized Graphene Quantum Dots as Photosensitizers. J Nanosci Nanotechnol 20(6):3432–3436
- 174. Majumder T, Mondal SP (2019) Graphene quantum dots as a green photosensitizer with carbon-doped ZnO nanorods for quantum-dot-sensitized solar cell applications. Bull Mater Sci 42:1–5
- 175. Gatti T, Manfredi N, Boldrini C, Lamberti F, Abbotto A, Menna E (2017) A D-π-A organic dye–Reduced graphene oxide covalent dyad as a new concept photosensitizer for light harvesting applications. Carbon 115:746–753
- 176. Zamiri G, Bagheri S (2018) Fabrication of green dye-sensitized solar cell based on ZnO nanoparticles as a photoanode and graphene quantum dots as a photo-sensitizer. J Colloid Interface Sci 511:318–324
- 177. Yeh MH, Lin LY, Su JS, Leu YA, Vittal R, Sun CL, Ho KC (2014) Nanocomposite Graphene/Pt Electrocatalyst as Economical Counter Electrode for Dye-Sensitized Solar Cells. ChemElectroChem 1(2):416–425
- 178. Xue Y, Liu J, Chen H, Wang R, Li D, Qu J, Dai L (2012) Nitrogen-doped graphene foams as metal-free counter electrodes in high-performance dye-sensitized solar cells. Angew Chem Int Ed 51(48):12124–12127
- 179. Yang W, Xu X, Li Z, Yang F, Zhang L, Li Y et al (2016) Construction of efficient counter electrodes for dye-sensitized solar cells: Fe2O3 nanoparticles anchored onto graphene frameworks. Carbon 96:947–954
- Li Z, Gong F, Zhou G, Wang ZS (2013) NiS2/reduced graphene oxide nanocomposites for efficient dye-sensitized solar cells. J Phys Chem C 117(13):6561–6566
- 181. Kavan L, Yum JH, Grätzel M (2011) ACS Nano 5:165-172
- Choi H, Kim H, Hwang S, Choi W, Jeon M (2011) Dye-sensitized solar cells using graphene-based carbon nano composite as counter electrode. Sol Energy Mater Sol Cells 95(1):323–325
- Zhang DW, Li XD, Li HB, Chen S, Sun Z, Yin XJ, Huang SM (2011) Graphene-based counter electrode for dye-sensitized solar cells. Carbon 49(15):5382–5388
- 184. Wang H, Sun K, Tao F, Stacchiola DJ, Hu YH (2013) 3D honeycomb-like structured graphene and its high efficiency as a counter-electrode catalyst for dye-sensitized solar cells. Angew Chem Int Ed 52(35):9210–9214
- Kavan L, Yum JH, Grätzel M (2011) Graphene nanoplatelets outperforming platinum as the electrocatalyst in co-bipyridinemediated dye-sensitized solar cells. Nano Lett 11(12):5501–5506
- Ma J, Li C, Yu F, Chen J (2014) 3 D Single-Walled Carbon Nanotube/Graphene Aerogels as Pt-Free Transparent

Counter Electrodes for High Efficiency Dye-Sensitized Solar Cells. ChemSusChem 7(12):3304–3311

- 187. Battumur T, Mujawar SH, Truong QT, Ambade SB, Lee W, Han SH, Lee SH (2012) Graphene/carbon nanotubes composites as a counter electrode for dye-sensitized solar cells. Curr Appl Phys 12:e49–e53
- 188. Li S, Luo Y, Lv W, Yu W, Wu S, Hou P et al (2011) Vertically Aligned Carbon Nanotubes Grown on Graphene Paper as Electrodes in Lithium-Ion Batteries and Dye-Sensitized Solar Cells. Adv Energy Mater 1(4):486–490
- Yang Z, Liu M, Zhang C, Tjiu WW, Liu T, Peng H (2013) Carbon nanotubes bridged with graphene nanoribbons and their use in high-efficiency dye-sensitized solar cells. Angew Chem Int Ed 52(14):3996–3999
- Sarker S, Lee KS, Seo HW, Jin YK, Kim DM (2017) Reduced graphene oxide for Pt-free counter electrodes of dye-sensitized solar cells. Sol Energy 158:42–48
- 191. Wei L, Wang P, Yang Y, Luo R, Li J, Gu X et al (2018) Facile synthesis of nitrogen-doped reduced graphene oxide as an efficient counter electrode for dye-sensitized solar cells. J Nanopart Res 20:1–12
- 192. Mohan K, Bora A, Roy RS, Nath BC, Dolui SK (2019) Polyaniline nanotube/reduced graphene oxide aerogel as efficient counter electrode for quasi solid state dye sensitized solar cell. Sol Energy 186:360–369
- 193. Kim H, Choi H, Hwang S, Kim Y, Jeon M (2012) Fabrication and characterization of carbon-based counter electrodes prepared by electrophoretic deposition for dye-sensitized solar cells. Nanoscale Res Lett 7:1–4
- 194. Yeh MH, Lin LY, Sun CL, Leu YA, Tsai JT, Yeh CY et al (2014) Multiwalled carbon nanotube@ reduced graphene oxide nanoribbon as the counter electrode for dye-sensitized solar cells. J Phys Chem C 118(30):16626–16634
- 195. Tsai CH, Shih CJ, Chou YR, Chi WF, Huang WC, Yu YH (2018) Preparation of reduced graphene oxide/macrocyclic manganese complex composite materials as counter electrodes in dye-sensitized solar cells. Org Electron 52:51–60
- 196. Velten J, Mozer AJ, Li D, Officer D, Wallace G, Baughman R, Zakhidov A (2012) Carbon nanotube/graphene nanocomposite as efficient counter electrodes in dye-sensitized solar cells. Nanotechnology 23(8):085201
- 197. Dissanayake MAKL, Kumari JMKW, Senadeera GKR, Jaseetharan T, Weerasinghe J, Anwar H (2021) A low-cost, vein graphite/tin oxide nanoparticles based composite counter electrode for efficient dye-sensitized solar cells. Mater Sci Eng B 273:115440
- 198. Jiang T, Yang S, Dai P, Yu X, Bai Z, Wu M et al (2018) Economic synthesis of Co3S4 ultrathin nanosheet/reduced graphene oxide composites and their application as an efficient counter electrode for dye-sensitized solar cells. Electrochim Acta 261:143–150
- 199. Dissanayake MAKL, Kumari JMKW, Senadeera GKR, Anwar H (2021) Low cost, platinum free counter electrode with reduced graphene oxide and polyaniline embedded SnO2 for efficient dye sensitized solar cells. Sol Energy 230:151–165

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