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Graphene-based 2D materials for rechargeable batteries and hydrogen production and storage: a critical review

Chandra Sekhar Bongu, Sehar Tasleem, Mohan Raj Krishnan and Edreese Housni Alsharaeh *

Batteries and hydrogen energy devices are considered the most critical technologies for achieving zero carbon dioxide emissions. However, they still suffer from several limitations, including low efficiency, short cycling life, low storage, and poor safety. With their strong mechanical strength (flexibility), chemical inertness, large surface area, remarkable thermal stability, and excellent electrical and high ion conductivity, graphene can overcome some of the issues associated with batteries and hydrogen energy devices. The properties of various two-dimensional (2D) materials make them potential candidates for a wide range of applications (batteries and hydrogen energy devices), thereby gaining considerable interest. Similarly, graphene has the potential for efficient hydrogen production and storage because of its large surface area and adjustable porosity. Graphene/2D composite materials are promising electrodes for lithium batteries, hydrogen storage, and production applications. This review provides a comprehensive overview of graphene/2D composite materials for lithium batteries and hydrogen storage and production applications.

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1. Introduction

The expanding population and growing industrialization have increased the need for energy globally to an unprecedented degree. However, most of our energy comes from fossil fuels, which increase greenhouse gas emissions (GHGs) and contribute to worldwide climate change.[1–4] The rising temperature of the earth's has prompted scientists to explore alternative energy sources. Reducing the dependency on fossil fuels and utilizing renewable energy to build new technologies are urgent. As a result, hydrogen (H_2) and batteries are considered clean and sustainable energy sources for the future.[5–12]

Batteries can store intermittent energy; thus, they are becoming increasingly popular as renewable sources.[13–15] Lithium-ion batteries are the most researched rechargeable batteries owing to their excellent energy density and storage capacity, which are advantageous for various applications and daily energy demands.[16–21] Electrode materials are crucial to lithium rechargeable batteries, but the sluggish kinetics and significant volume changes still hinder further applications.[16,22–24]

H_2 is an effective and clean energy source that substitutes fossil fuels.[25–27] Hydrogen energy has a gravimetric density roughly seven times higher than that of fossil fuels.[28] Hydrogen, a readily available element and a flexible energy carrier, can transform several industries and sectors, including manufacturing, transportation, and power generation. The potential of hydrogen to provide energy without producing hazardous pollutants makes it significant. Since water is the only byproduct of using hydrogen as fuel, hydrogen is a clean and green choice.[29] However, even with its enormous promise, there are still some obstacles that must be overcome before hydrogen energy is widely used.[30] The main issues are linked to the production and storage of H_2 energy.[31] Regarding H_2 production, novel catalysts and materials, such as nanostructured catalysts, are being investigated to speed up reactions and increase the efficiency for maximizing hydrogen generation.[29] Furthermore, the lower volumetric density of hydrogen necessitates huge storage capacities or high pressure. Therefore, advanced catalysts and materials can significantly improve the efficacy and effectiveness of hydrogen storage.[32] The common materials used to store hydrogen energy are sodium aluminium hydride ($NaAlH_4$), lithium aluminium hydride ($LiAlH_4$), lithium borohydride ($LiBH_4$), magnesium nickel hydride (Mg_2NiH_4), sodium borohydride ($NaBH_4$), aluminium hydride (AlH_3), zeolites, metal–organic frameworks (MOFs), and covalent organic frameworks (COFs).[33–40] However, the drawback of hydrogen adsorption–desorption exists as it lacks reversibility because of its strong bonding force and slow kinetics, necessitating high temperatures for desorption. For the production of hydrogen, titanium dioxide (TiO_2), molybdenum disulfide (MoS_2), tungsten(VI) oxide (WO_3), zinc oxide (ZnO), iron oxide (α-Fe_2O_3), bismuth vanadate ($BiVO_4$), copper

College of Science and General Studies, AlFaisal University, PO Box 50927, Riyadh, 11533, Saudi Arabia. E-mail: ealsharaeh@alfaisal.edu

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oxide (Cu_2O), cadmium sulfide (CdS), and copper/zinc/tungsten (Cu/Zn/W) sulfide are widely employed as electrodes.[41–48] However, certain stability and low-efficiency challenges persist, leading to their poor photoelectrochemical (PEC) activity for hydrogen production.[49,50] Thus, innovative strategies are needed to address these issues and increase hydrogen generation methods' safety, economy, and efficiency.

Lithium-ion batteries, hydrogen storage, and production electrode material capabilities are found in several carbon-based substrates including porous carbons (PCs), carbon nanotubes (CNTs), MXenes and nanofibres (NFs) with different geometries.[51–56] Among all the recently discovered and synthesized nanostructured carbonaceous species, graphene stands out as the most extraordinary material. Their remarkable properties including their enormous surface area, mechanical toughness, and electrical conductivity have revolutionized the study of materials. Consequently, compared to other carbon compounds (PCs, CNTs, MXenes, and NFs), graphene has been used advantageously as prospective substitute electrode materials in many applications for improving particular technical domains, particularly those related to energy generation and storage. Because of their large theoretical SSA (2630 $m^2\ g^{-1}$) and ease of functionalization by heteroatoms such as N atoms, graphene offers more electrochemical reaction active sites than other carbon compounds (PCs, CNTs, MXenes, and NFs).

Graphenes were isolated in 2004 and used in energy storage due to their high thermal conductivity, high electrical conductivity, high elasticity and flexibility, and high hardness. Particularly in lithium-ion batteries, they serve as electrodes, conductive materials, and controllers for volume expansion in the electrode material. However, Li ions may ideally be accommodated on both sides of graphene, and their theoretical capacity is at least double that of other carbon-based materials (PCs, CNTs, MXenes, and NFs).[57,58] The graphene is a promising substitute for improving H_2 generation efficiency. Because of graphene's particular two-dimensional conjugated framework and electrical characteristics, it can be used to increase the photocatalytic efficiency.[59] Moreover, the graphene, composed of carbon atoms arranged in a honeycomb lattice, holds the potential for hydrogen storage, giving rise to new hopes for creating an effective solid-state hydrogen storage device.[60] In recent years, several papers have been published on graphene composites with 2D materials in batteries and hydrogen storage and production applications. This review aims to assess graphene composites with 2D materials for lithium batteries, hydrogen storage, and production applications.

2. Lithium rechargeable batteries

2.1 Graphene-based 2D materials for lithium-ion batteries (LIBs)

2.1.1. Graphenes for lithium-ion batteries (LIBs). Numerous portable devices that are essential to modern life are powered by rechargeable batteries. Rechargeable battery technologies with high power and energy densities are also currently being investigated for the electrification of autos.[61,62] The market for rechargeable batteries used for energy storage is dominated by LIBs, a type of battery that operates on the intercalation and de-intercalation of Li ions due to many fascinating features, such as high energy and power density, long cycle life, low self-discharging, and no memory effect.[63] As seen in Fig. 1, lithium-ion batteries typically consist of the following four components: the cathode, anode, electrolyte, and separator.[64] Graphitic materials are typically used as the anode material in commercial LIBs, while Li metal oxides or phosphates such as $LiCoO_2$ and $LiFePO_4$ are commonly used as the cathode material.[65] A separator keeps the chemical potentials of the cathode and anode apart. During the charging and discharging processes, Li ions can flow between the cathode and the anode *via* an organic electrolyte based on carbonate, including a salt containing Li, such as lithium hexafluorophosphate ($LiPF_6$). During discharging, electrons move from the anode to the cathode while Li ions move through the electrolyte to keep the charge balanced. An external electrical power source forces the electrons and Li ions to go in the opposite direction during the charging process.

"Anode" refers to the negative electrode that releases an electron into the external circuit. An anode collects lithium ions and converts them into active materials. Some characteristics that the anode materials should have include a large energy capacity, excellent charge/ion storage, ion release, long cycle rate, ease of manufacture, safety in use, and cost-effectiveness.[67] Since the early 1990s, Sony has been commercially launching LIBs, with graphite was the anode material. Currently, graphite, the most popular anode material in LIBs, has a relatively low theoretical capacity of about 372 mA h g^{-1} and safety issues related to the insertion of Li^+ into the anode structure.[68] A graphite anode's limited capacity will prevent it from meeting the demands of the rapidly expanding industries.[69] To improve LIB performance and energy density, research is required to fabricate new anode materials with a capacity greater than that of graphite.[70]

A 2D nanomaterial called graphene is made up of hexagon-shaped carbon atoms with sp^2 hybrid orbitals. Graphene has garnered considerable interest across numerous applications since its isolation in 2004.[71–77] Graphene, a single layer of

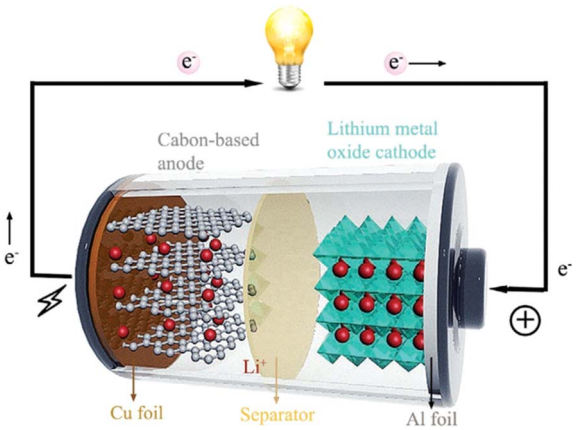

Fig. 1 Schematic of the structure and working mechanism of LIBs.[66]

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graphite, is attracting a lot of attention as a potential anode material due to its enormous specific surface area (2620 m^2 g),[78] mechanical strength, excellent thermal conductivity (5000 W m^{-1} K^{-1}),[79] electrical conductivity, rapid charge–discharge cycles and a more remarkable ability to hold Li ions and higher capacity (three times that of graphite).[80–83] Because of its high energy storage capacity of 669 mA h g^{-1}, good cycling stability, longer interlayer distance of 0.615 nm with mild van der Waals forces, and simple intercalation and deintercalation procedure, graphene is highly suitable for LIB anode applications.[84] Numerous scientists have noted that Li^+ ion attachments may be facilitated by extra paths provided by graphene sheet defects. The enormous challenge of fabricating LIBs that can provide high power and energy density outputs during charging and discharging may have an answer in this feature. However, porous graphene's high ionic conductivity, surface characteristics, and electric conductivity have attracted considerable attention in battery research.[85] Ordered mesoporous graphene nanosheets were synthesized by Fang *et al.* using a regulated low-concentration mono micelle close-packing assembly technique.[86] This anode can hold 833 mA h g^{-1} at different current densities after multiple cycles. It can give a high reversible capacity of 1040 mA h g^{-1} at 100 mA g^{-1}. About 255 mA h g^{-1} of reversible capacity is kept even at a high current density of 5 A g^{-1}. For instance, magnesium oxide and methane were used as starting ingredients in the chemical vapor deposition process to synthesize a hierarchical porous graphene nanomaterial. The Brunauer–Emmett–Teller (BET) surface area and pore size were changed, and this affected the electrochemical properties of LIBs.[87] In particular, the heteroatom-doped graphene has demonstrated advances in the electrochemical performance of LIBs. Using the differential electroneutrality of doped nitrogen (N), phosphorus (P), sulfur (S), and boron (B) heteroatoms, a method was devised to increase the relative specific capacity (900 mA h g^{-1}) of LIBs.[81,88–92] However, extensive research has revealed that the ionic-steric effect and decreased stability of graphene make it impractical to use it directly as an anode active material in LIBs.[93,94] Furthermore, with several advantageous effects, the synthesis of graphene-based composites has been one of the most important avenues for LIB anode active materials. The graphene, particularly with a 2D material, has emerged as a potential anode active material for LIB applications.

2.1.2. Graphene/graphitic carbon nitride (C_3N_4) anodes for lithium-ion batteries. Because of their comparable layered architectures, graphene and graphitic carbon nitride (C_3N_4) are known to be modifiable. Synergistic effects between graphene and g-C_3N_4 are caused by highly exposed N-active sites on conductive graphene sheets, which increase the electrochemical characteristics. Nevertheless, these active spots become inactive as soon as graphene aggregation occurs. Thus, structural exploration of g-C_3N_4/graphene-based materials could help design a stable 2D structure with many active sites. Shuguang Wang *et al.* prepared a g-C_3N_4@reduced graphene oxide composite (g-C_3N_4@RGO) in a cost-effective way and applied it as an LIB anode (Fig. 2a).[95] For practical applications, the coin-type half batteries are fabricated with g-C_3N_4@RGO and connected in series to a tandem red light-emitting diode (LED) and a watch. The g-C_3N_4@RGO electrode delivered a stable cycle performance with a 595.1 mA h g^{-1} capacity even after 1000 cycles at a high current density of 1 A g^{-1}. Marlies Hankel and co-workers designed a C_3N_4/graphene heterostructure and conducted scanning electron microscopy (SEM) analysis to observe its morphology (Fig. 2b). However, the Density Functional Theory (DFT) study showed superior conductivity of the designed C_3N_4/graphene heterostructure for LIB applications. The C_3N_4/graphene heterostructure electrode exhibited an excellent electrochemical capacity of 862.2 mA h g^{-1} after 90 cycles with a coulombic efficiency of 90.4%.[96]

2.1.3. Graphene/hexagonal boron nitride (h-BN) for lithium-ion batteries. With its strong mechanical strength, chemical inertness, remarkable thermal stability, and high ion conductivity, h-BN has emerged as a potential solution for various energy storage and conversion issues. Generally speaking, h-BN can function as an ideal modifier to increase battery safety by enhancing separators' mechanical strength, providing superior thermal conductivity, and prolonging the cycle life of Li-metal batteries by safeguarding the solid-state electrolyte. During charge–discharge cycling, lithium metal experiences a constant growth of Li dendrites, which results in low coulombic efficiency and early failure. After extensive cycle experiments, John Hong *et al.* reported a freestanding h-BN nanosheet separator with exceptional physical rigidity against dendritic Li development and exceptional thermal endurance in high-temperature settings.[100] Pol *et al.* prepared bilayer separators and used them in lithium-ion batteries. A polypropylene (PP) membrane covered with a layer of boron nitride-graphene (BN_xGr_y) dramatically lowers polarization and impedance while greatly enhancing cell performance and stability. The full cell fabricated with the modified BN_xGr_y/PP separator delivered a discharge capacity of 114 mA h g^{-1} at 1C rate even after 1000 cycles (Fig. 2e).[97] Using the Hall potentiometry approach, Frank Zhao *et al.* reported the electrochemical intercalation of Li into graphene enclosed between h-BN layers (Fig. 2c).[98] This work presents an electrochemical method for the controlled intercalation of lithium ions into a range of van der Waals heterostructures composed of hexagonal boron nitride and graphene. Tong Teo and colleagues successfully made the composite films of reduced graphene oxide (rGO)/boron nitride (BN) using simple vacuum filtration and subsequent heat treatment (Fig. 2d).[99] The thin 2D nanosheet morphologies of rGO and BN were well retained following their combination, according to the morphological analysis of the generated rGO/BN SEM images. The electrochemical analysis indicates that the composite film electrode with rGO/BN (rGO/BN-2%) exhibits superior rate performance. Even at a high current density of 1 A g^{-1}, the rGO/BN (rGO/BN-2%) electrode delivers a specific capacity of 121 mA h g^{-1}, which is higher than that of the rGO film electrode.

2.1.4. Graphene/transition metal dichalcogenides (TMDs) for lithium-ion batteries. Because of their unique lamellar structure, TMDs have a superior electrochemical active interface, excellent mechanical properties, higher specific capacity,

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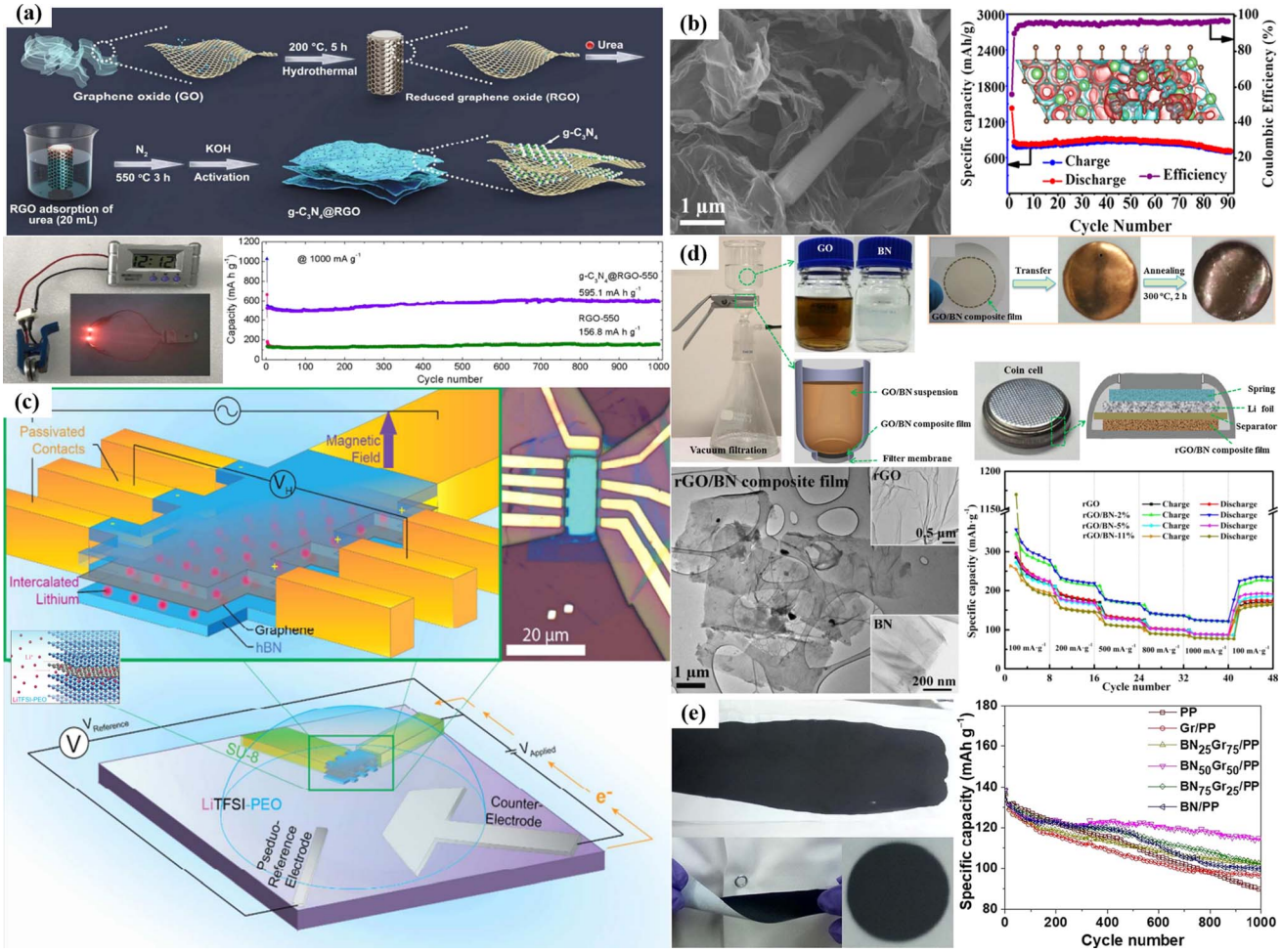

Fig. 2 (a) Schematic of the synthesis procedure of g-C_3N_4@RGO. (b) SEM image and DFT calculations of the C_3N_4/graphene heterostructure. (c) Hall bar device with the h-BN/graphene/h-BN heterostructure. (d) Vacuum filtration process for preparation, transmission electron microscopy (TEM) image and electrochemical study of the GO/BN composite film. (e) Bilayer BN_xGr_y/PP separator and electrochemical characterization of LIBs.[95–99]

and improved cycling stability compared to typical carbon anodes, and hence, LIBs frequently use them. However, TMDs are a viable option for energy storage applications because of their huge intercalation gap, which can encourage the quick interlayer migration of lithium ions. TMDs have the structure MX_2, where X can be either tellurium (Te), selenium (Se), or S, and M can be any transition metal element (*e.g.*, titanium (Ti), tungsten (W), vanadium (V), and molybdenum (Mo)). Typical two-dimensional TMDs are molybdenum disulfide (MoS_2), vanadium sulfide (VS_2), vanadium selenide (VSe_2), tungsten disulfide (WS_2), and so forth. The obstacles of the TMDs for commercial application volume expansion and during the charge–discharge process are the van der Waals interaction between TMD sheets, which lowers the utilization rate. TMDs with layered structures such as graphene are easier to exfoliate and facilitate quick ion diffusion. With its huge specific surface area, great mechanical capabilities, and excellent electrochemical stability, TMD/graphene heterogeneous composites are perfect energy storage materials. The hollow MoS_2 nanocages/RGO nanocomposites fabricated by Dafang He *et al.* are assembled using a straightforward solvothermal-assisted assembly technique in conjunction with freeze-drying and annealing (Fig. 3a).[101] The graphene and MoS_2 are tightly bound *via* molecular links, contributing to the structural stability, improved electrical conductivity, and increased lithium storage capacity of the MoS_2 anode material. Thus, at a high current density of 3 A g^{-1} (Fig. 3b), this new nanocomposite demonstrates good rate capability and significant potential as an anode nanocomposite for improved lithium-ion batteries. By a simple hydrothermal process, Xinglan Zhou *et al.* fabricated 1T MoS_2 nanosheets on graphene oxide (GO) as an anode in lithium-ion batteries. The synthesized 1T MoS_2/GO (1 g) electrode exhibited the first specific charging/discharging capacity of 1612 mA h g^{-1} at a current density of 0.1 A g^{-1}. It maintained a specific capacity of 774 mA h g^{-1} even after 60 cycles at a current density of 1 A g^{-1}.[105] WS_2 one more TMD was reported for lithium-ion battery anode materials due to its excellent electrochemical properties.[106] Yong-Lin Wu *et al.* synthesized a WS_2/graphene nanosheet composite *via* ball milling followed by calcination to overcome the van der Waals interactions

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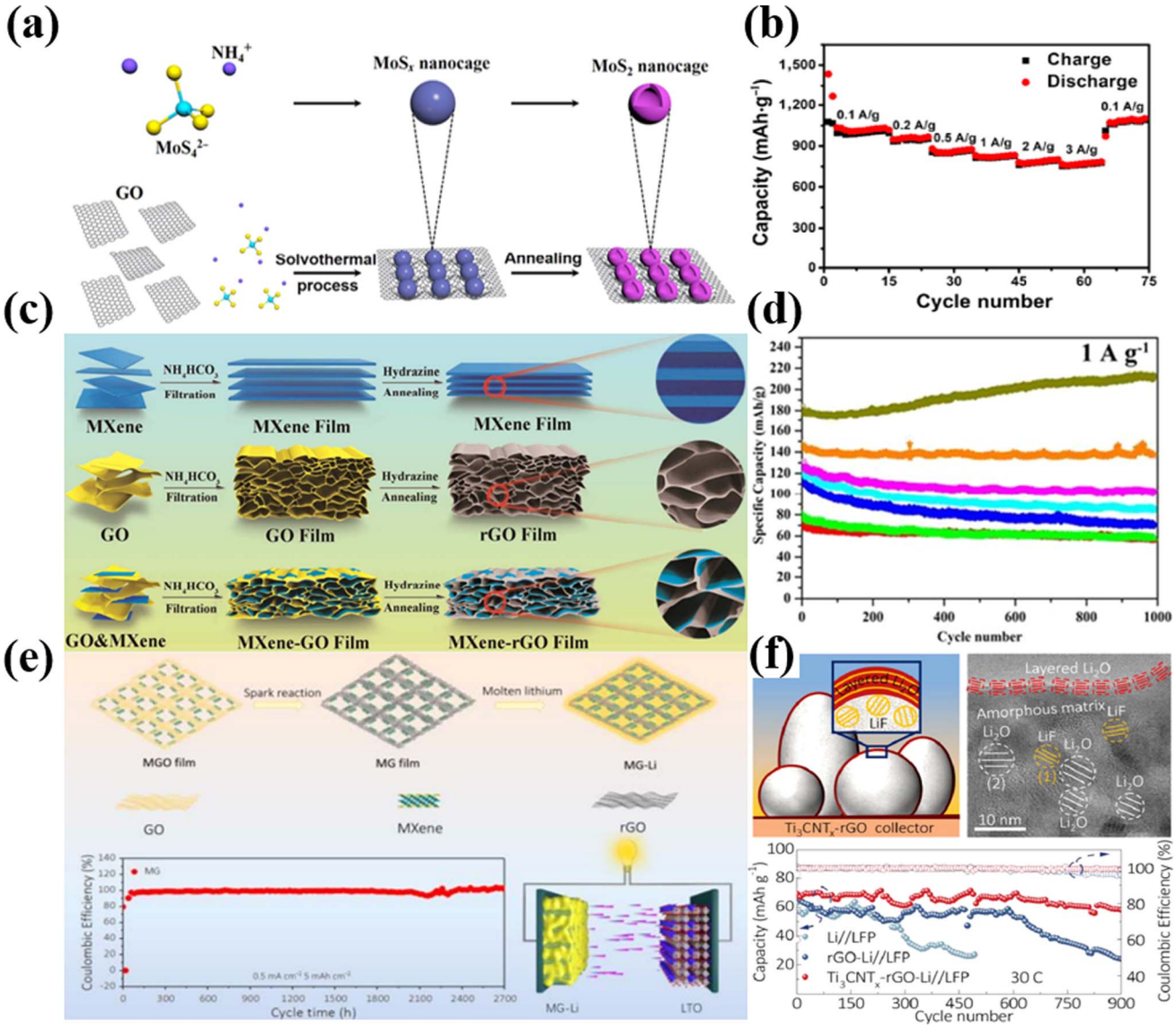

Fig. 3 (a) Synthesis process and (b) rate performance of the MoS_2/RGO nanocomposite and MoS_2 electrode. (c) Fabrication and (d) electrochemical performance of the MXene, rGO and MXene-rGO films at 1 A g^{-1}. (e) Fabrication and coulombic efficiencies of the MG electrode at a current density of 0.5 mA cm^{-2} with a Li deposition amount of 5 mA h cm^{-2} for 2700 h. (f) Lithiophilic functional groups result in the formation of a uniform SEI layer (decomposition of $LiN(CF_3SO_2)_2$); cryo-TEM images of equally dispersed LiF and ordered layered Li_2O and superior cycling lifespan over 900 cycles with a capacity retention of 77.7% at 30C of Ti_3CNT_x/G/Li electrode.[101–104]

between the interlayer of graphite and WS_2.[107] At a current density of 250 mA g^{-1}, the produced WS_2/GNS composite anode material exhibited a 95% capacity retention rate and a high reversible specific capacity of 705 mA h g^{-1} even after 200 cycles.

2.1.5. Graphene/MXenes for lithium-ion batteries. Another class of electrode materials that have recently attracted much attention are MXenes. MXenes is a collective term for a novel class of 2D carbonitride, nitride, and carbide materials that was coined in 2011. MXenes have demonstrated significant promise in using LIB electrodes due to their distinct 2D structure and abundant active sites on their surface. However, the noticeable restacking effects of MXene layers and low electric conductivity cannot be used in battery applications. Thus, MXenes combined with graphene composites have proven to be highly effective electrodes for Li-ion batteries, and they have been successfully fabricated. Yun-Ting Du *et al.* methodically examined the electrochemical characteristics of MXene/graphene heterostructures and their potential applications in energy storage through first-principles calculations.[108] The results show that adding graphene improves the mechanical stiffness, Li adsorption strength, and electric conductivity and prevents the restacking effects of MXene layers. Zhiying Ma *et al.* synthesized a MXene (titanium carbide (Ti_3C_2)) and graphene hybrid film in different ratios and applied it for lithium-ion storage applications (Fig. 3c).[102] The hybrid film has a high specific capacity of 335.5 mA h g^{-1} at 0.05 A g^{-1} and is used as an electrode material for lithium-ion batteries. Because of its stable structure, the film electrode also shows good cycling

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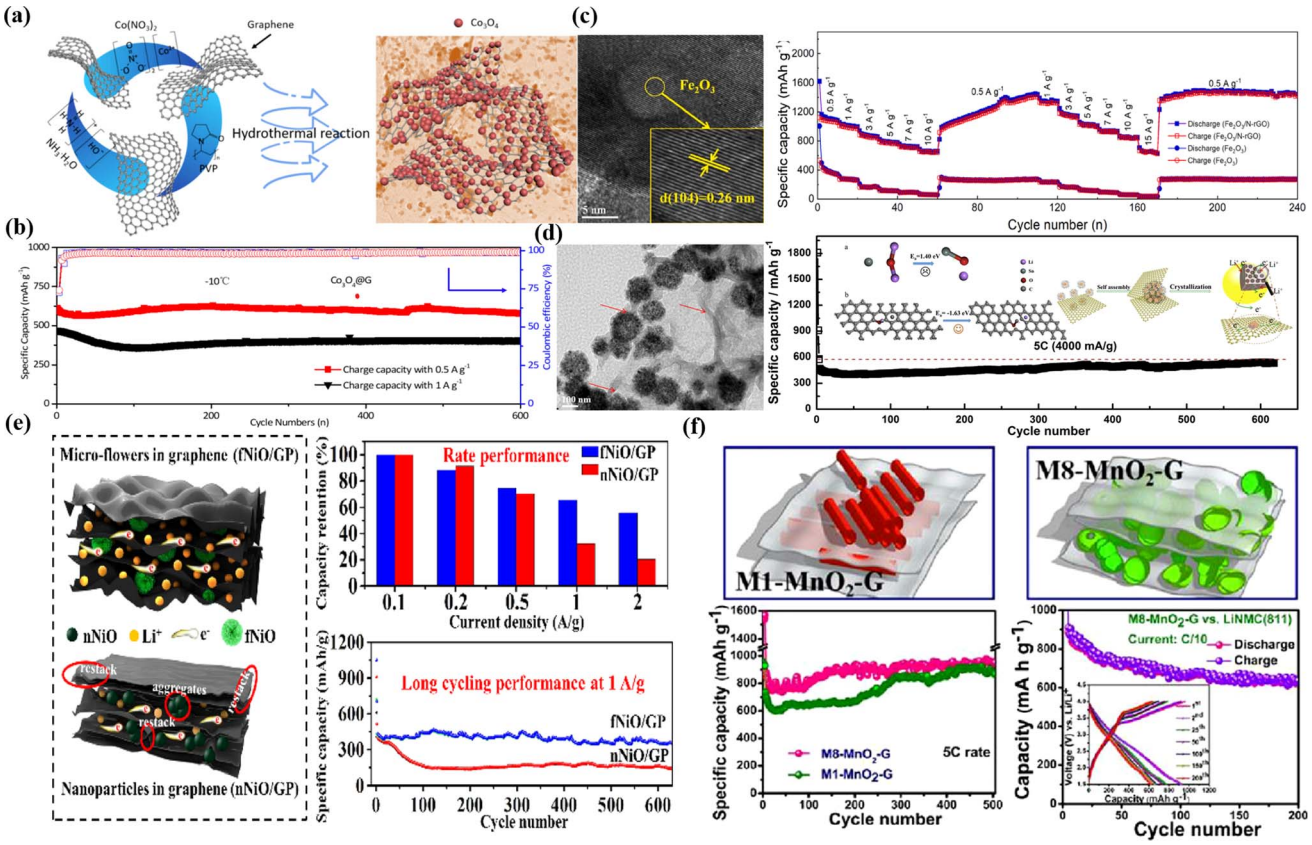

Fig. 4 (a) Schematic representation of the preparation and (b) long-cycling performance of Co_3O_4@G at −10 °C and different current rates. (c) High-resolution transmission electron microscopic (HRTEM) image of the Fe_2O_3/N-rGO sample and rate capability of Fe_2O_3/N-rGO and pure Fe_2O_3 at different current densities. (d) TEM image and long cycling performance of the SnO_2@graphene sponges (GS) at a current density of 5C. (e) NiO micro-flowers/graphene paper electrode rate capability at different current densities and long cycling at 1 A g^{-1}. (f) Long cycling performance of the M1-MnO_2-G and M8-MnO_2-G composite anode material and full cell study of the M8-MnO_2-G composite anode with the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode.[118–122]

stability, with no capacity loss even after 1000 cycles at high rates (1 A g^{-1}) (Fig. 3d). However, MXenes/graphene also use a dendrite-free Li metal anode in lithium-ion batteries. The synthesized MXene/graphene electrode by Zhong-Shuai Wu and colleagues has a record lifespan of 2700 hours and high coulombic efficiency of ∼99% (Fig. 3e).[103] Comparably, the conductive scaffold was employed by MXene (Ti_3CNT_x) and graphene composites to control Li nucleation and solid-electrolyte interphase (SEI) production on the Li metal anode. With a capacity retention of 77.7% at 30C, the Ti_3CNT_x-G-Li electrode-based complete cells with $LiFePO_4$ have an exceptional cycling lifespan of over 900 cycles (Fig. 3f).[104] Carbon nanotubes (CNTs) and graphene with varying weight ratios of MXene to carbon, synthesized by Motahare S. Mohseni-Salehi *et al.*, were hybridized with the nanohybrids.[109] With a coulombic efficiency of 98%, the V_2CT_x MXene/G showed an impressive specific discharge capacity of 460 mA h g^{-1} at a current rate of 100 mA g^{-1}.

2.1.6. Graphene/transition metal oxides (TMOs) for lithium-ion batteries. Over the past few decades, transition metal oxides (TMOs) have been the subject of extensive research because of their intriguing charge transfer and storage properties. However, TMOs as LIB anodes are still far from commercial applications due to noticeable volume expansion (∼300%) observed during the cycling process. To improve the anode material's performance and get around these problems, TMOs and graphenes can be combined.[110,111] The graphene is an ideal conductive carbon coating for TMO anode materials to mitigate the volumetric expansion.[112] Therefore, to overcome the aforementioned drawback, a number of methods have been proposed as practical solutions for extending the cycle life and reducing the volume expenditure of LIB anode materials. One such method is the preparation of nanocomposite materials, which capitalize on the synergy between combined materials.[113–116] By a straightforward sonication process, MnO_2 nanotubes were able to integrate the components *via* the electrostatic interaction of the MnO_2 nanotubes and graphene functional groups. It was discovered that the incorporation of graphene oxide improved the interfacial characteristics and structural stability during charge/discharge cycling while reducing volume expansion and charge transfer resistance.[117]

Cobalt oxide (Co_3O_4) has been studied as an anode material since it was first used as the anode electrode for LIBs because of its advantages, which include a large theoretical specific

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capacity of approximately 890 mA h g^{-1}, wide availability, ease of manufacture, and stable chemical properties. Liang Tan *et al.* used a simple hydrothermal method to make a Co_3O_4/graphene composite, which was subsequently tested at very low temperatures (Fig. 4a).[118] The Co_3O_4/G anode exhibits a noticeably higher capacity of 605 mA h g^{-1} at 0.5 A g^{-1} (Fig. 4b) than that of other anodes at temperatures below zero thanks to the material's creative nanostructure, high conductivity, and extremely good lithiation and delithiation potentials. The inexpensive metal oxide Fe_2O_3 can displace graphite as the primary anode material for lithium-ion batteries. The redox conversion reaction from Fe_2O_3 to a combination of Li_2O and metallic iron gives a theoretical capacity of up to 1006 mA h g^{-1}. Yu Huang *et al.* used a simple and effective one-pot hydrothermal process to create a 2D nanostructured Fe_2O_3/N-rGO composite (Fig. 4c). When tested as LIB anodes, the 2D nanostructured Fe_2O_3/N-rGO composite demonstrated an exceptional high-rate capacity of 652 mA h g^{-1} at 15 A g^{-1} (Fig. 4c).[119] A similar Fe_2O_3/multilayer graphene was synthesized by Junming Xu *et al.* by a chemical deposition method, which when used as the anode for LIBs exhibited a specific capacity of 1050 mA h g^{-1} at 0.1C even after 100 cycles.[123] Due to their noteworthy characteristics, tin oxide (SnO_2) nanoparticles have been thoroughly investigated for various energy-related applications, including LIBs. Naiqing Zhang and coworkers reported hierarchical SnO_2 nanoclusters anchored on the graphene sponges (SnO_2/GS) *via* a solvothermal approach with an average diameter of ~110 nm, as shown in Fig. 4d.[120] These hierarchical SnO_2/GSs retained a higher reversible capacity of 600 mA h g^{-1} after over 600 cycles at 4000 mA g^{-1} (Fig. 4d). Based on a conversion reaction from nickel oxide (NiO) to metallic nickel and Li_2O, the estimated theoretical capacity for NiO is 718 mA h g^{-1}. The NiO also suffers from poor rate performance and cycling stability similar to those of other conversion-based anode nanomaterials. NiO composite with graphene is used in the LIB applications to address these obstacles. Ju Fu *et al.* synthesized hierarchically porous NiO micro-flowers/graphene papers (fNiO/GP) by a facile hydrothermal method followed by annealing in air at 400 °C for 40 min (Fig. 4e).[121] Even after 600 cycles at a current density of 1000 mA g^{-1}, fNiO/GP demonstrated high reversible specific capacities of 359 mA h g^{-1} in lithium-storage applications (Fig. 4e). Similarly, graphene–(Ni–NiO)–C hybrid was hydrothermally treated at 180 °C for 24 h and then carbonized at 700 °C for three hours by Jian-Guo Zhao and colleagues.[124] When it was used as the anode material for LIBs, the initial capacity was 711.6 mA h g^{-1}, and after 300 cycles, it increased to 772.1 mA h g^{-1}. Manganese dioxide (MnO_2) is plentiful in the Earth's crust, which is a more environmentally friendly metal oxide than other oxides. As an anode for LIBs, MnO_2 has a high theoretical capacity of 1232 mA h g^{-1}, enabling a quick charge/

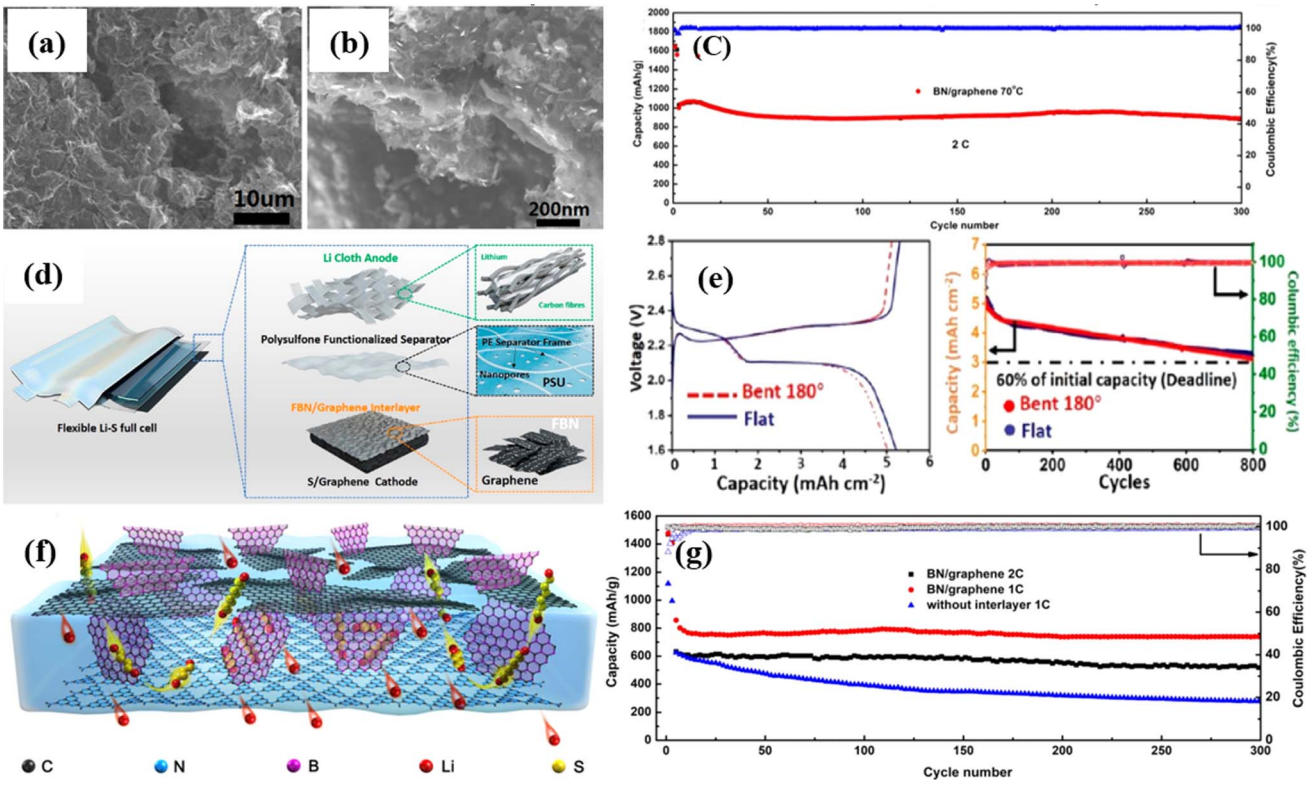

Fig. 5 (a and b) SEM images of BN/graphene. (c) Long cycling performance of BN/graphene at 70 °C temperature. (d) Lithium cloth anodes, PSU-Celgard separators, and free-standing graphene/sulfur cathodes shielded by an FBN/G interlayer are used to build flexible Li–S complete cells. (e) Charge/discharge curves and cycling performance of the Li–S pouch cells in the flat state and bent state, respectively, of the FBN/graphene interlayer. (f) Scheme of the multi-functional ion-sieve constructed by three 2D materials (gC_3N_4, BN and graphene). (g) Coulombic efficiency and discharge capacity of the cell with the BN/graphene interlayer at rates of 1C and 2C.[127–129]

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discharge rate over a broad potential window. As anode materials for Li-ion batteries, Pedda Masthanaiah Ette *et al.* revealed that two distinct mesoporous MnO_2 were produced from silica templates (MCM-41 and MCM-48) and integrated with graphenes (Fig. 4f).[122] Both composites demonstrate improved rate performance, large discharge capacity, and strong cycling stability. When used as LIB electrodes, M8-MnO_2-G exhibits a consistent discharge capacity of 1494 mA h g^{-1} at a rate of 5C (Fig. 4f). The synergistic effects of graphene-integrated mesoporous MnO_2 are responsible for the composites' high specific capacities and long cycling performance. $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ as a cathode studied the full cell tests with an M8-MnO_2-G composite material anode. The full cell shows a stable capacity up to 200 cycles at a current density of 0.1C.[122]

2.2 Graphene-based 2D materials for lithium–sulfur batteries (LSBs)

Lithium–sulfur batteries are considered the most promising candidates among the battery technologies now used to act as the batteries of the future generation with superior electrochemical performance. The high specific capacity (~1675 mA h g^{-1}) and high energy density (~2600 W h kg^{-1}) of lithium–sulfur batteries (LSBs) have gained interest in recent years.[125] The present bottlenecks of LSBs include the severe shuttle effect of soluble lithium polysulfides (LiPSs) and slow redox kinetics, which lead to capacity fading and poor rate performance.[126] Due to the severe capacity fading (poor cycling stability) and low coulombic efficiency that these devices exhibit, the effective practical implementation of these devices has been put off. Numerous approaches have been proposed to address these problems, some of which involve using 2D-based materials to produce a better component architecture, as will be covered in the following discussion.

2.2.1. Graphenes/hexagonal boron nitride (h-BN) for lithium–sulfur batteries. With its Li-friendly surface and high stability, h-BN can reduce Li dendrites without sacrificing the Li-ion conductivity. Furthermore, h-BN can act as Lewis acidic sites to attract polysulfide anions in the electrolyte, increasing the Li–S battery capacity. Thanks to their synergistic impact, h-BN and graphenes have been validated as improved cathode materials in LSBs. This combination can efficiently adsorb LiPSs and speed up the redox kinetics for LiPS conversion, even under challenging conditions. According to Deng *et al.*, the G/BN composite cathode demonstrated a capacity fading <0.04% per cycle at 70 °C and reached a steady capacity of 888 mA h g^{-1} at 2C after 300 cycles. However, graphene/BN is also constituted by functional separators or interlayers blocking barriers for LiPS in LSBs. Recently, an extremely flexible LSB with a cathode made of graphene/sulfur composites, an anode made of lithium cloth, an interlayer made of functionalized BN nanosheets and graphenes, and a separator made of functionalized polysulfone have also been produced (Fig. 5a–c).

Consequently, the resulting flexible Li–S full-cells exhibit excellent electrochemical performance at a high areal capacity of 5.13 mA h cm^{-2} and a high volumetric and gravimetric energy density of 468 W h L^{-1} in the folded state, up to 800 cycles (Fig. 5d and e). In contrast to separators, an efficient interlayer must have a high conductivity to maximize the use of active sulfur and boost rate capability. With a polypropylene membrane covered with g-C_3N_4/h-BN/G, the LSB was built, and after 500 cycles at 1C, it released a discharge capacity of around 600 mA h g^{-1}. The capacity attenuation was less than 0.01% per cycle with a 6 mg cm^{-2} area S-loading (Fig. 5f and g).

2.2.2. Graphene/graphitic carbon nitride for lithium–sulfur batteries. The organic n-type visible light-active semiconductor graphitic carbon nitride (g-C_3N_4) photocatalyst attracted a lot of attention in various applications due to its 2D structure, composition devoid of metals, and excellent chemical and thermal stability. Strong affinity to Li_2S_n is demonstrated by graphitic carbon nitride (g-C_3N_4), a 2D structure similar to graphene, which is explained by the chemical interaction between Li atoms and pyridinic-N sites. Juan Zhang *et al.* used a microemulsion technique to fabricate a 3D porous sulfur/graphene@g-C_3N_4 (S/GCN) hybrid sponge that may be used as a cathode for Li–S batteries with improved electrochemical characteristics. The outcomes of these combined effects are superior performances of 3D S/GCN in terms of high specific capacity, advantageous high-rate capability, and exceptional long-term cycling stability. Specifically, a low-capacity fading rate of 0.017% per cycle over 800 cycles at 0.3C and a high energy density of up to 1493 W h kg^{-1} are attained.[130] Furthermore, this one-pot method is straightforward to use. It eliminates the need for unwanted Li_2S_n catalysts, which simplifies the process of creating sulfur/carbon hybrid electrodes (Fig. 6a and b). Significantly, in another study published by Qu, Long, *et al.*, polysulfides were trapped using the 2D g-C_3N_4/graphene sheet composite (g-C_3N_4/GS) as an interlayer for a sulfur/Ketjen black carbon (S/KB) cathode. The interlayer of g-C_3N_4/GS combined with the sulfur-based cathode produced an exceptionally high reversible capacity of 1191.7 mA h g^{-1} at 0.1C after 100 cycles, which is significantly greater than the reversible capacity of the sulfur-based cathode alone (625.8 mA h g^{-1}). It also demonstrated extended cycling stability with a reversible capacity of 612.4 mA h g^{-1} at 1C after 1000 cycles (Fig. 6c and d).[131] Xiaoyu Wu *et al.* group synthesized an S@C-NC/GN/g-C_3N_4 cathode and performed electrochemical characterization at a rate of 0.5C. After 500 consecutive electrochemical cycles, the manufactured S@C-NC/GN/g-C_3N_4 cathode exhibits an outstanding cycling performance, maintaining a high reversible capacity of around 1130 mA h g^{-1} (Fig. 6e and f).[132]

2.2.3. Graphenes/MXenes for lithium–sulfur batteries. MXene is a 2D transition metal carbide or carbonitride emerging from the MAX phase. Many sulfur atoms can be loaded into the unusual structural variation of MXenes, and the addition of heteroatoms increases the chemisorption of polysulfide. Furthermore, the material's superior electrical conductivity and lithium-ion transport capacity enable its direct application as a sulfur carrier. The electrochemical performance of the LSBs can be noticeably enhanced with the MXene@S cathode. Engineered MXenes can help with material agglomeration and stacking issues, but the procedure is highly time-consuming and costly. Consequently, scientists have improved the MXene carbon composite material.[133–135] Ti_3C_2 is

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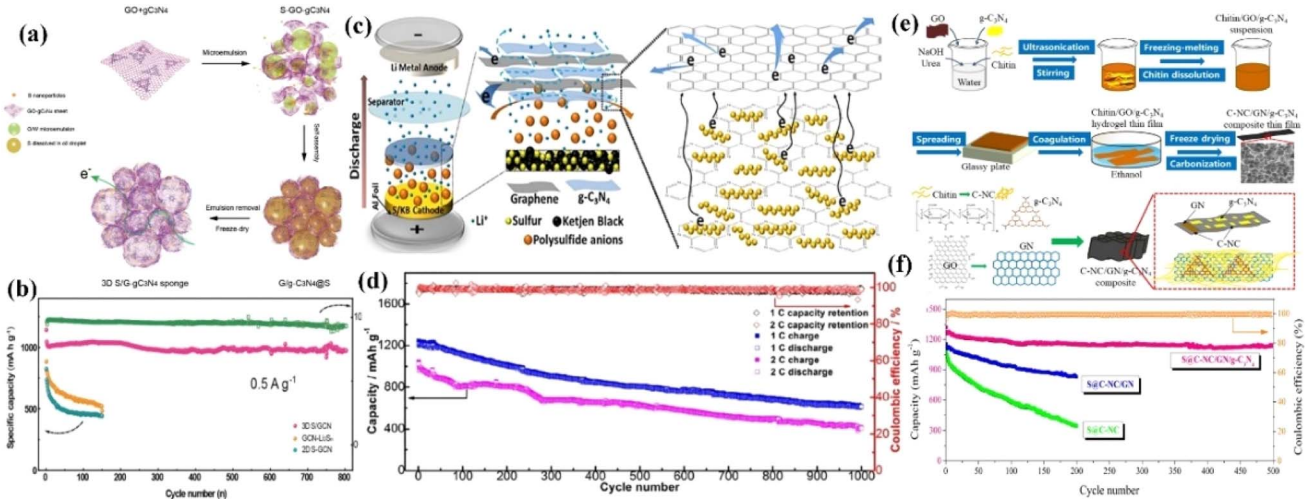

Fig. 6 (a) Schematic of the procedure for preparing S/GCN hybrid sponge. (b) Long-term cycling performance of S/GCN, GCN-Li_2S_n, and S-GCN cathodes at a low current density of 0.5 A g^{-1} (0.3C). (c) Schematic of cell configuration with a laminated structure of the g-C_3N_4/GS cathode interlayer. (d) Cycling performance and capacity retention of the S/KB@C_3N_4/GS cathode at 1 and 2C for 1000 cycles. (e) Free-standing 3D network cathode (N-doped carbon/graphene/g-C_3N_4) preparation. (f) Long cycling performance of the S@C-NC, S@C-NC/GN and S@C-NC/GN/g-C_3N_4 cathodes at 0.5C rate.[130–132]

the MXene derivative that is investigated most frequently among all of the them.[136] According to Luo Yuanzheng *et al.*, a freestanding graphene-supported N-doped $Ti_3C_2T_x$ MXene@S cathode was successfully manufactured by the co-assembly of rGO flakes onto the sulfur particles in a reduction process *via* a simple sacrificial templating approach (Fig. 7a). The battery was able to achieve a high specific capacity of 721.7 mA h g^{-1} at 0.1C and a capacity retention of 579.6 mA h g^{-1} after 300 cycles with the optimal N–$Ti_3C_2T_x$@S/G cathode despite a comparatively high loading amount of 5.2 mg cm^{-2} (Fig. 7b).[137] A functionally antagonistic Janus composite made of sulfur, graphene oxide, and $Ti_3C_2T_x$ MXene was reported by Sanghee Nam *et al.*[138] While the GO side offers significant porosity and nonelectrical conductivity, the MXene side retains mechanical qualities and

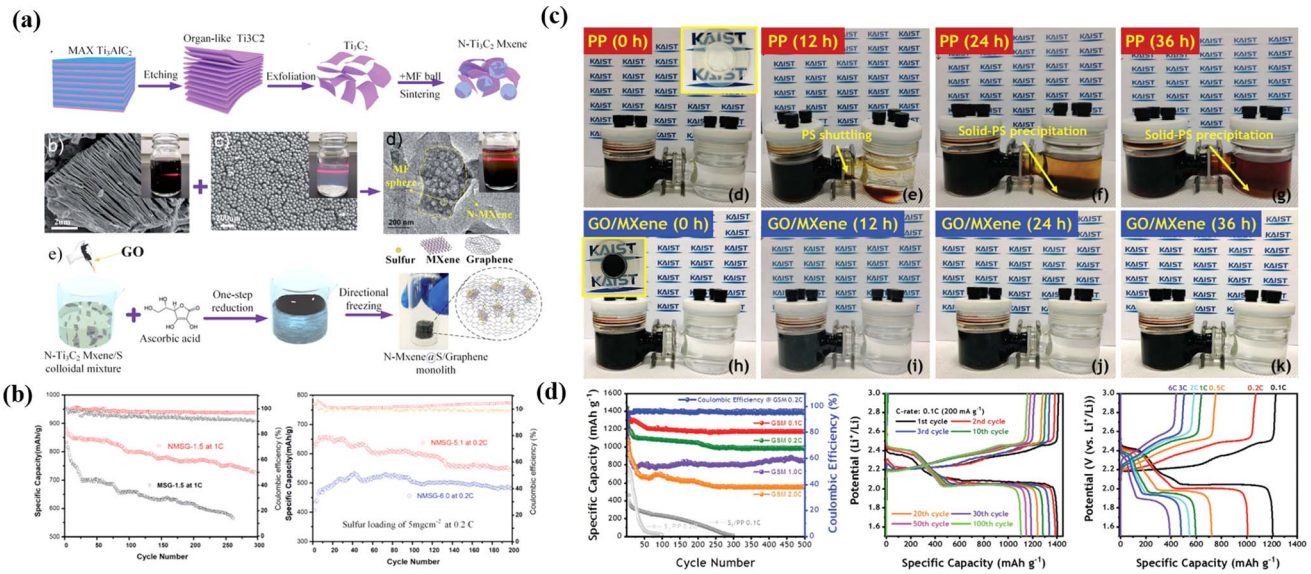

Fig. 7 (a) Schematic of the synthesis of N–$Ti_3C_2T_x$ MXene nanosheets; corresponding SEM and TEM images of $Ti_3C_2T_x$ flakes, the melamine–formaldehyde (MF) nanosphere and the $Ti_3C_2T_x$-wrapped MF nanosphere and schematic of the one-step synthesis process of the freestanding NMXene@S/G composite. (b) Long-term cycling performances of the Li–S cell with NMSG at 1C for 300 cycles. (c) Optical images of the visualized lithium polysulfide diffusion test with a commercially available PP separator and a GO/MXene bilayer composite at 0, 12, 24, and 36 h, consisting of Li_2S_6 (Left), GM (Middle), and DOL/TEGDME (Right) in a H-type electrolytic cell and electrochemical measurements; long-term cycling test at 0.1, 0.2, 1.0, and 2.0C of GSM and S8/PP cell. (d) Charge–discharge profile at a C rate of 0.1C (200 mA g^{-1}) from the 1st to the 100th cycle; charge–discharge profiles at different C rates (0.1 to 6C).[137,138]

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metallic-like conductivity. As a result, GO and MXenes were employed as the selective separator and current collector, respectively. The permselectivity test in a 50 mL H-type electrolytic cell with a GO/MXene bilayer composite (GM) and a commercial PP separator is shown in Fig. 7c. The color of these two cells' right chambers was assessed after 12, 24, and 36 hours. Dark brown gradually altered in the right chamber using a PP (Fig. 7c). As seen in Fig. 7c, however, in the instance of the GM, LiPSs did not diffuse to the right chamber, and the right chamber's color remained colorless. As seen in Fig. 7d, the charge–discharge tests were carried out at different current densities ranging from 0.1 to 2.0C. With a cyclic retention of around 85.1%, the specific capacity demonstrated exceptional stability at low C rates. The particular capacities at 1.0 and 2.0C were adequately maintained despite minor variations. At 0.1 and 0.2, respectively, the initial discharge capacities were 1424.52 and 1241.67 mA h g^{-1}. At different C rates of 0.2, 0.5, 1.0, 2.0, 3.0, and 6.0C, respectively, specific capacities of 1, 046.73, 731.85, 617.86, 461.3, and 422.94 mA h g^{-1} were achieved (Fig. 7d).

2.2.4. Graphenes/transition metal dichalcogenides for lithium–sulfur batteries. Transition metal dichalcogenides (TMDs) with layered structures such as graphenes are easier to exfoliate and facilitate quick ion diffusion. TMDs exhibit multiple structural phases, with the most prevalent in the octahedral (1T) and trigonal prismatic (2H) phases. Numerous new characteristics are present in these various TMD groupings. As a result, they have been extensively employed in studying different ion battery electrode materials. In recent years, TMD and TMD/graphene composite materials have brought new life to the design of LSBs for enhanced performance. He *et al.* fabricated a graphene/1T-MoS_2 heterostructure with high-efficiency electrocatalytic properties, suppressing the polysulfide shuttle, to enhance the performance of LSBs. A few layers of graphene nanosheets were sandwiched between metallic, hydrophilic 1T-MoS_2 multilayers with many active sites to form the heterostructure (Fig. 8a). While a high conductivity of 1T-MoS_2 and graphene facilitates electron transmission, the porous 3D structure and hydrophilicity aid in the electrolyte penetration and Li-ion transfer. As shown in Fig. 8b, these benefits result in the graphene/1T-MoS_2-containing LSBs having good electrochemical performance, with a reversible discharge capacity of 1181 mA h g^{-1} and a capacity retention of 96.3% after 200 cycles.[139] Similarly, $MoTe_2$@-graphene composites were prepared quickly and easily *via* microwave synthesis by Zhen Wei *et al.* and utilized as cathode host materials for LSBs to reduce polysulfide shuttling and enhance interfacial electron/ion transport. The $MoTe_2$@-graphene@carbon cloth electrode demonstrated exceptional rate performance, good cycling stability (98.7% capacity retention after 100 cycles at 0.2C), and a high initial discharge capacity of 1246 mA h g^{-1} at 0.2C for the first galvanostatic cycle (Fig. 8c).[140] A MoS_2@ carbonized melamine foam (CF)-nitrogen-doped reduced graphene oxide (NRGO) composite was fabricated by Jiayu Zhan *et al.* and used in Li–S batteries as a modified polypropylene separator layer (MoS_2@CF-NRGO/PP) (Fig. 8d). The composite preserved a three-dimensional carbon matrix structure, which improved Li^+ shuttling conditions and improved the LiPS filtration efficiency (Fig. 8e–g). Li–S batteries featuring a separator modified by MoS_2@CF-NRGO demonstrated an exceptional rate performance of 615 mA h g^{-1} at 5C, surpassing the CF-NRGO and PP configurations (Fig. 8l).

Additionally, after 200 cycles, the MoS_2@CF-NRGO modified separator exhibits a 99.6% average coulombic efficiency, demonstrating an outstanding capacity retention. After ten charge/discharge cycles at 0.5C, Li–S batteries were allowed to rest for five days to examine their self-discharge behavior. Following a five-day rest period, the MoS_2@CF-NRGO configuration's discharge capacity drops from 1015.8 to 927.9 mA h g^{-1}, with an average self-discharge value of only 8.6% (Fig. 8l). The molybdenum disulfide/graphene (MoS_2/G) interlayer was constructed by Mingang Zhang and his team using a straightforward coating technique, and it was utilized in an LSB separator.[142] The color change of the mixed solution can be used to directly compare and evaluate the polysulfide adsorption capacity of composites (Fig. 8m). At 0.1C, the CNT/S@MoS_2/G cathode has an initial discharge capacity of 1537.2 mA h g^{-1}. At 0.5C, the CNT/S@MoS_2/G cathode has a discharge capacity of 984.9 mA h g^{-1} (Fig. 8n). With an ultralow capacity decay of 0.061% every cycle, the capacity drops to 713.8 mA h g^{-1} after 450 cycles. The CNT/S@MoS_2/G cathode delivered excellent rate capability. The MoS_2/G interlayer, which sits between the cathode and the separator, is thought to have more excellent cycling stability because it confines polysulfide to the cathode and lessens the shuttle effect.

2.2.5. Graphenes/transition metal oxides for lithium–sulfur batteries. Metal oxide-decorated graphenes both reduce the shuttle effect that polysulfides cause and improve their chemical adsorption, because of their strong surface polarity. As a result, research on graphene and metal oxide complex composites has been extensive. A double-shelled TiO_2–graphene heterostructure (H–TiO_2/rGO) with a high degree of exposure on the active plane and a lot of oxygen vacancies has been described by Yanqi Feng *et al.* as an enhanced host material for LSBs.[143] The electrode (S–TiO_2/rGO-1) combines the beneficial properties of strong anchoring and catalysing LiPSs to provide a product with excellent rate performance, a long lifespan (1000 cycles at 1C, 0.023% capacity loss per cycle), and high coulombic efficiency (Fig. 9a). The polysulfide shuttle in the LSBs was regulated by the thin TiO_2/graphene interlayer, as demonstrated by Zhubing Xiao *et al.* (Fig. 9b).[144] It was discovered that the porous carbon nanotube (PCNT)–S cathode could provide a reversible specific capacity of ≈1040 mA h g^{-1} over 300 cycles at 0.5C thanks to the application of the graphene/TiO_2 sheet as an interlayer (Fig. 9c). Porous graphenes provided an extra electrically conducting network and physically confined S and PS in this well-thought-out design. As an added benefit, TiO_2 in the graphene/TiO_2 barrier film further chemically suppressed PS's dissolution and lessened the undesired shuttle effect. Youlong Xu group reported that ferric oxide nanoparticles on an N, S co-doped graphene (Fe_3O_4–N, S/rGO) sheet structure may have a major impact on the development of Li–S batteries with high energy density and extended cycling life by

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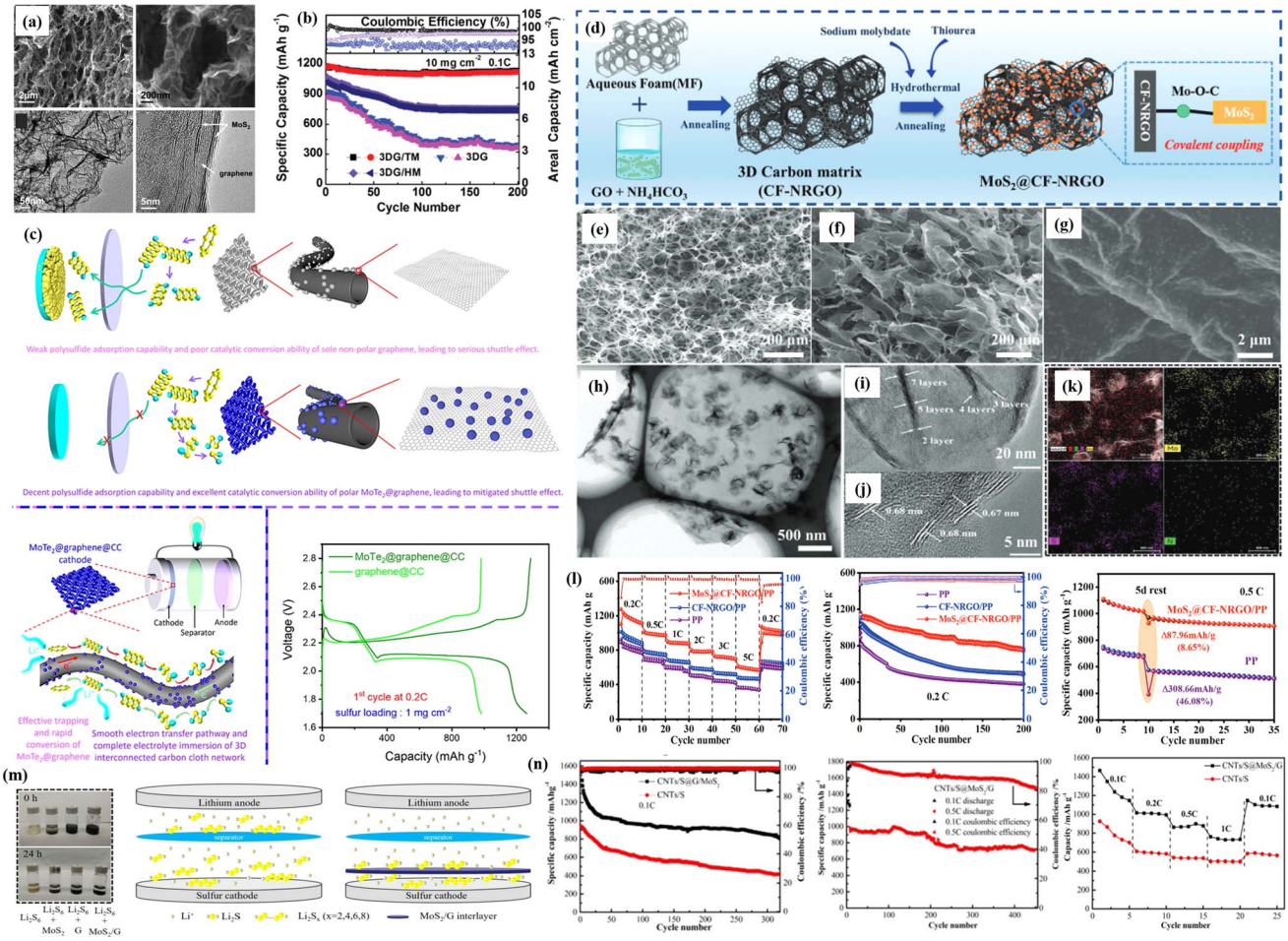

Fig. 8 (a) SEM images of 1T MoS_2 on the graphene aerogel ((three-dimensional graphene) 3DG/1T MoS_2 (TM)). (b) Cycling stability of electrocatalytically active 3DG, 3DG/1H MoS_2 (HM), and 3DG/TM as working electrodes *vs.* Li/Li^+ with a catholyte consisting of 1 M Li_2S_6 at 0.1C rate.[139] (c) Polysulfide conversion ability of polar $MoTe_2$@graphene composite as a cathode material for LSBs.[140] (d) Schematic of the preparation stages of MoS_2@CF-NRGO. SEM images of (e) carbonized MF and (f and g) MoS_2@CF-NRGO. (h) TEM and (i and j) HR-TEM images of MoS_2@CF-NRGO. (k) EDS mapping images of MoS_2@CF-NRGO and the corresponding images of Mo, S, and N. (l) Rate capacity and cycling capabilities at 0.2C of a cell with the MoS_2@CF-NRGO/PP separator, CF-NRGO/PP, and PP separators and cycling performance at 0.5C before and after rest of the MoS_2@CF-NRGO/PP and PP separators,[141] (m) digital photographs of MoS_2 and MoS_2/G composites in a Li_2S_6 solution for 0 and 24 h; schematic of the lithium–sulfur battery without and with the MoS_2/G interlayer. (n) Cycling performance and coulombic efficiency of the carbon nanotube (CNT)/S@MoS_2/G and CNT/S cathodes at 0.1C, cycling performance and coulombic efficiency of the CNT/S@ MoS_2/G at 0.5C and rate capability.[142]

controlling LiPSs and improving the conversion kinetics.[145] Using a straightforward microwave hydrothermal process (Fig. 9d), ferric oxide nanoparticles on an N, S co-doped graphene (Fe_3O_4–N, S/rGO) sheet structure were fabricated and used as the cathode for LSBs. In the end, the built Fe_3O_4–N, S/rGO–S batteries provide consistent long-term cycle life and high-rate capability. The Fe_3O_4–N, S/rGO–S electrode continues to provide a high discharge specific capacity of 1004 mA h g^{-1} even after 200 cycles at 0.5C (Fig. 9e).

2.3 Graphene-based 2D materials for lithium–O_2 and lithium–CO_2 batteries

Rechargeable Li–O_2 and Li–CO_2 batteries, which offer a higher theoretical energy density than that of Li-ion batteries, have recently attracted a lot of attention.[146,147] Li–O_2 batteries have been developed to fulfil the increased demand for electric energy in today's world. The formation of a lithium peroxide (Li_2O_2) product, which has a substantially higher energy storage capacity than that of other energy storage systems, is responsible for the high energy density of Li–O_2 batteries.[148] The high band gap of solid Li_2O_2, which is probably covering the catalytic sites, makes charge transfer necessary for the breakdown of Li_2O_2 during the charge process difficult.[149] This results in a slow charging process that raises the potentials needed for Li_2O_2 breakdown, which lowers the battery's energy efficiency and increases the danger of electrolyte degradation.[150,151] Furthermore, the size and shape of the Li_2O_2 product can affect the charge potential. Developing Li–O_2 batteries requires improving the materials used in each component of the battery in order to address knotting problems. Two-dimensional materials have recently attracted attention due to their

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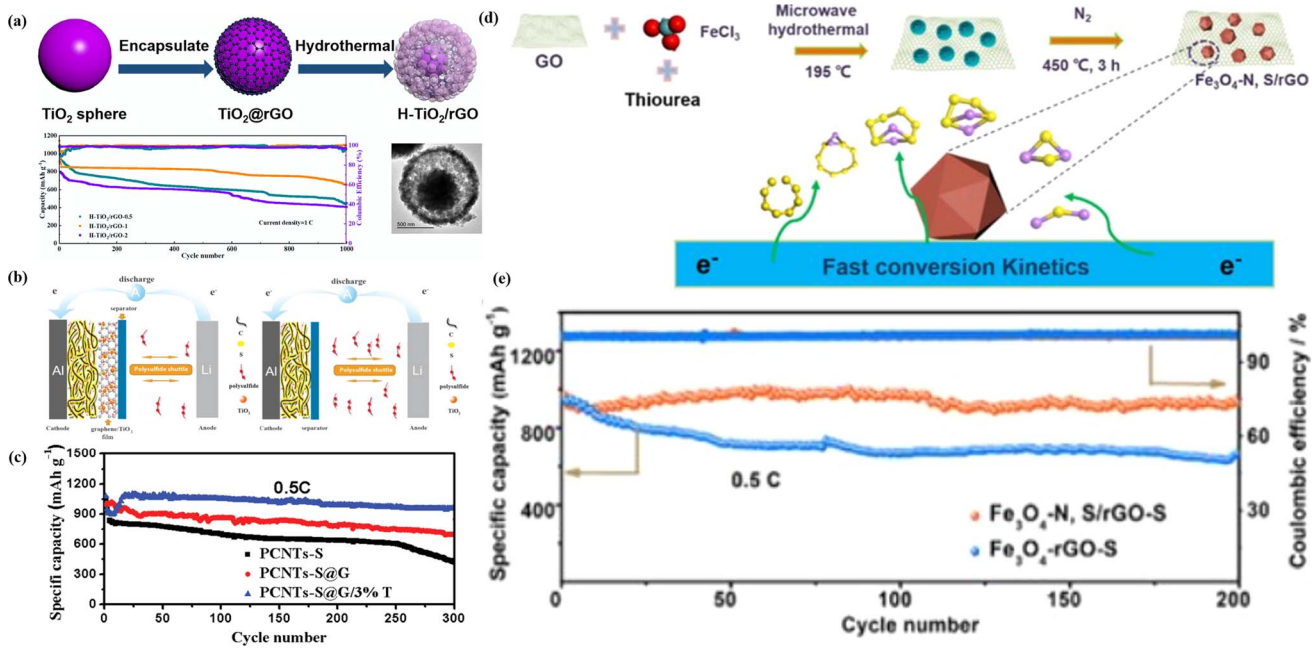

Fig. 9 (a) Schematic of the formation and long-term cycling performances at a current density of 1C of H–TiO_2/rGO-1.[143] (b) Schematic of the electrode configuration for the Li–S battery with a graphene/TiO_2 coating film and conventional Li–S battery. (c) Cycling stability of PCNTs–S, PCNTs–S@G, and PCNTs–S@G/3% TiO_2 cathodes at 0.5C, and a current density of 0.86 mA cm^{-2}.[144] (d) Schematic of the synthesis process of the Fe_3O_4–N, S/rGO composite. (e) Cycling performance of the Fe_3O_4–N, S/rGO–S and Fe_3O_4-rGO–S electrode at 0.5C after 200 cycles.[145]

potential to improve the Li–O_2 battery performance. This is because of their distinct designs, which have the potential to effectively address a number of issues related to the electrode materials (cathode and anode), solid-state electrolyte, and separator in Li–O_2 batteries.[152–155] A unique type of MnO_2@rGO nanocomposite material was described by Lihua Zhu *et al.*; it is very effective for Li–O_2 batteries and consists of extremely few nano-sized MnO_2 grains on the surface of rGO (Fig. 10a). In Li–O_2 batteries, MnO_2@rGO composites were used as cathode catalysts with a cut-off capacity of 1000 mA h g^{-1} and a current density of 200 mA g^{-1} (Fig. 10b).[156] Over 60 cycles, batteries based on MnO_2@rGO demonstrated a consistent discharge capacity. Strong synergistic effects between the rGO framework and the nano-sized MnO_2 particles on its surface are responsible for the exceptional performance. Functionalized graphenes with an optimal bimodal porous structure were produced by Jie Xiao *et al.* for Li–O_2 battery operation (Fig. 10c). A novel air electrode that uses an uncommon hierarchical configuration of functionalized graphene sheets produces the highest capacity of 15 000 mA h g^{-1} at around 2.7 V.[85] Yuejiao Li and colleagues described the facet engineering of an ultrathin, two-dimensional Mn_3O_4 nanosheet on graphene (Mn_3O_4 NS/G) with the dominating (101) crystal planes. The goal of this catalyst is to generate durable, effective oxygen for high-performance Li–O_2 batteries that exhibit ultrahigh capacity and long-term stability, offering a lower charge overpotential (Fig. 10d).[157]

Similar to Li–O_2 batteries, the Li–CO_2 battery is another advanced technology because of its high theoretical energy density of 1876 W h kg^{-1}. Li–CO_2 batteries offer a novel method for capturing CO_2 and advancing the development of electrochemical energy storage systems of the next generation by using CO_2 as the active material at the cathode. Rechargeable Li–CO_2 batteries store energy by breaking down the discharge products when exposed to external electricity during the charging process. During discharge, this process produces electricity *via* a redox reaction between the Li anode and the CO_2 cathode, namely Li_2CO_3.[159–161] Zhang Zhang *et al.* reported the first introduced graphene as a cathode material to improve the performance of Li–CO_2 batteries.[162] Wei Yu *et al.* synthesized N, O-diatomic graphene carbon aerogels by a straightforward, one-step thermal approach and used it as a cathode Li–CO_2 battery. The resulting Li–CO_2 batteries demonstrated an impressive cycling stability of more than 1500 h at 20 μA cm^{-2} and a significantly improved initial energy efficiency of about 78.46%.[160] MXene-based materials have been used as the cathode in Li–CO_2 batteries because of their superior interlayer ion transport channels, strong electrical conductivity, and chemical composition's tunability. Wentian Zhao prepared porous TVGA *via* a hydrothermal reaction and used it as a cathode in Li–CO_2 batteries (Fig. 10e). The TVGA cathode has flexible nature, and hence, a flexible Li–CO_2 battery was fabricated and used in different bending angles. Light-emitting diodes (LEDs) can be steadily lit by a Li–CO_2 battery without any adjustments (Fig. 10f). Fig. 10g compares the cycling performance of Li–CO_2 batteries with different cathodes. At a current density of 200 mA g^{-1}, TVGA displays a comparatively low overpotential of 1.5 V.[158] The battery has a 91 times stable cycling capacity at 200 mA g^{-1}, with an over potential of 1.5 V for both charging and discharging. These exceptional

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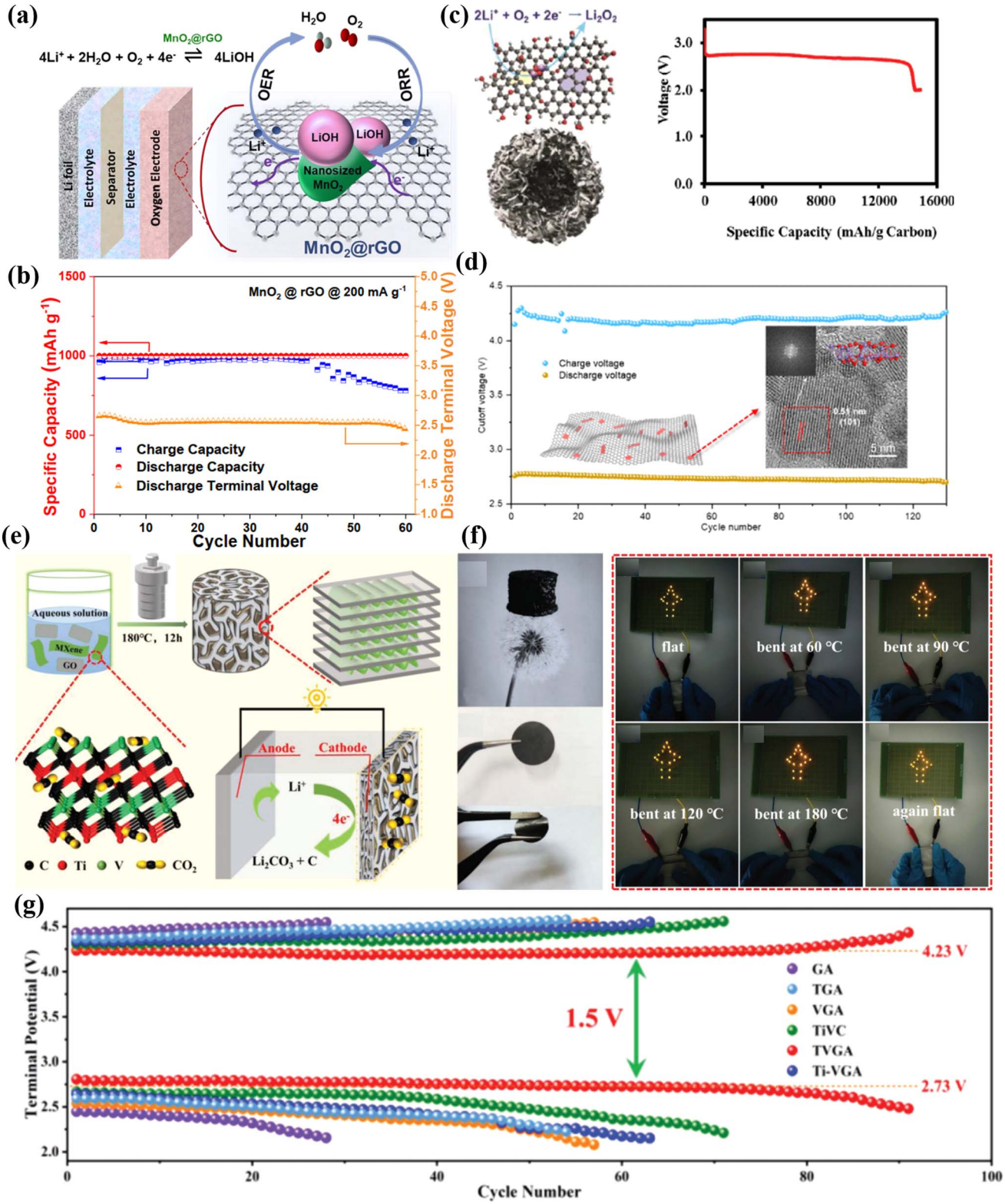

Fig. 10 (a) Schematic of the structure catalyzed by MnO_2@rGO for the Li–O_2 battery. (b) Discharge/charge capacity of MnO_2@rGO for the Li–O_2 battery at a current density of 200 mA g^{-1}. (c) An optimal bimodal porous structure on a functionalized graphene sheet (FGS) and the discharge curve of a Li–O_2 cell using the FGS. (d) Two-dimensional Mn_3O_4 nanosheets on graphene with charge/discharge voltages. (e) Li–CO_2 battery's schematic, optical picture and flexible optical picture of the TiVC/rGO aerogel (TVGA) cathode sheet. (f) LEDs with the flexible Li–CO_2 battery. (g) Variation in the terminal polarization of Li–CO_2 batteries with different cathodes at a current density of 200 mA h g^{-1}.[85,156–158]

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electrochemical performances are due to the special synergistic interaction between Ti and V in TiVC, which improves the reversible formation and breakdown of the discharge product Li_2CO_3 by enhancing the interfacial chemical bonding ability, realizing the full exposure of active sites and promoting the catalytic interfacial structural reorganization. In the meantime, the aerogel's rich pore structure helps lower the mass and charge transfer resistance by promoting the diffusion of CO_2 and electrolytes in addition to helping to enhance ion transport.

3. Lithium metal anode modification with graphenes

Since lithium metal has the lowest working potential (−3.04 *vs.* conventional hydrogen electrode) and the largest specific capacity (3860 mA h g^{-1}), it has been considered the best option for lithium-ion battery anodes. The lithium metal anode, a crucial component of the next generation of high-energy density lithium metal batteries (LMBs), has gained significant interest from both industry and academics. However, because of its innate propensity to generate dendrites during cycling, the lower cycling stability and safety concerns have long hindered the adoption of lithium metal anodes. The excessive parasitic interactions between the Li metal dendritic growth and the liquid electrolyte result in the irreversible consumption of both the electrolyte and active lithium. Consequently, the rapid capacity decline and catastrophic cell failure of LMBs are explained by the production of Li dendrites. Several methods have been devised to enhance the lithium metal anode's cycling stability and controlling the Li dendrites.[163–169] According to David Mitlin and colleagues, a significant degree of structural and chemical imperfection in graphene leads to unstable SEI formation. This is associated with the rapid decline of coulombic efficiency and the production of filament-like Li dendrites, as well as the consumption of the fluoroethylene carbonate (FEC) additive in the carbonate electrolyte.[164] Pinxian Jiang *et al.* described the graphene hybrid architecture as a lithiophilic host for a high-performance Li metal anode. They utilized it in the LMB to synthesize a nanosheet/graphene heterostructure composite *via* a polymer-assisted sonochemical process. The Li metal anode that results from the graphene hybrid architectural scaffold shows stable cycling over 200 cycles at 0.5 mA cm^{-2} (2 mA h) and provides a high energy density of 402 W h kg^{-1}.[170]

4. Hydrogen production and storage

4.1 Sustainable green hydrogen production approaches

Hydrogen (H_2) is recognized as an efficient energy carrier as it is an eco-friendly, non-toxic, renewable, and less costly energy source. Currently, H_2 is generated from renewable and non-renewable sources, where only 95% of H_2 is from non-renewable fossil fuels, and 5% is from renewable sources such as solar and wind.[41] The H_2 production approaches dependent on non-renewable resources are associated with CO_2 emissions, are expensive and energy-intensive, and involve harsh operating conditions.[171] Thus, researchers are exploring approaches to generate sustainable, less costly, and zero carbon-emitting H_2 energy.[172] In terms of renewable energy, the role of abundantly existing solar energy is significant, and two approaches for H_2 production can be employed, namely, (1) photocatalytic and (2) photoelectrochemical. Photocatalytic H_2 production by water splitting using semiconductor catalysts is a widely researched, less costly, eco-friendly, and effective approach for green H_2 generation.[173,174] Moreover, PEC water splitting for H_2 production is another approach that uses solar-irradiated photoelectrodes and an external bias voltage to suppress charge recombination, leading to excellent overall performance.[175]

4.1.1. Mechanism of photocatalytic and photoelectrochemical H_2 production. Generally, an efficient photocatalytic setup needs a catalyst capable of absorbing visible irradiation as a major part of sunlight constitutes irradiation within the visible range, a suitable photoreactor, and a sacrificial agent (Table 1).[191] Moreover, an effective interaction between all the components of the photocatalytic setup is needed for significant performance improvement.[192] Overall, water splitting into H_2 and O_2 is not favorable in terms of thermodynamics under normal temperature and pressure conditions because of the existence of strong bonds in H_2O and its low power to ionize. Therefore, at room temperature, the entire process needs 237 kJ mol^{-1}, *i.e.*, 2.46 eV per H_2O molecule of Gibbs free energy (ΔG).[193] The photocatalytic H_2 generation process initiates after the semiconductor catalyst absorbs the solar irradiation, having a wavelength greater than or equal to the semiconductor band gap to generate electron–hole pairs followed by the separation of charges where electrons jump to the conduction band (CB) of the semiconductor and holes are left in the valence band (VB). Then, a redox reaction occurs, where the electrons play a role in the reduction of H^+ to H_2, and the holes are responsible for oxidizing H_2O into O_2.[194] Eqn (1)–(3) describe the steps involved in overall photocatalytic H_2 generation. Moreover, for the photocatalytic process, the energy level of the semiconductor CB should be at a potential less than 0 V ($E(H^+/H_2)$) for the reduction process, and the VB energy level should be at a higher potential than 1.23 V ($E(O_2/H_2O)$) to conduct oxidation reactions.[195,196] Fig. 11a illustrates the photocatalytic H_2 generation mechanism over photocatalysts.

$$2H^+ + 2e^- \rightarrow H_2 \quad (1)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad (2)$$

$$2H_2O + 2O_2 \rightarrow 2H^+ \quad (3)$$

The PEC H_2 production utilizes a PEC cell comprising two or three electrodes acting as semiconductors for photoelectrodes submerged in an aqueous electrolyte, with the electrodes separated by a membrane.[195] Out of the electrodes used, one or two electrodes should have the potential to be activated under irradiation. Normally, the PEC comprises three electrodes for water splitting: a photoanode and a cathode act as active

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Table 1 Summary of the recent 2D graphene-based nanocomposites as photocatalysts for photocatalytic H_2 production together with the yield of H_2 and parameters, including loading of catalyst, source of light, and sacrificial agent

Photocatalyst	Catalyst loading (mg)	Light source	Sacrificial agent	H_2 production (μmol g^{-1} h^{-1})	Ref.
TiO_2/rGO/MoS_2	50	3 W 4 LEDs (λ 365 nm)	10 vol% methyl alcohol	880	176
2D CN@graphene@CN	10	300 W Xe lamp with 420 nm cut-off filter	10 vol% TEOA	5580	177
Few-layer graphene (FLG)/g-C_3N_4	0.15 g L^{-1}	4 LEDs of 880 W m^{-2} each (420 nm)	10% v/v ethylenediaminetetraacetic acid (EDTA) and 3 wt% Pt	1274	178
0D-2D-2D CdSe QD/B-rGO/O-gC_3N_4	30	Xe arc lamp (λ > 400 nm)	Triethanolamine (TEOA)	1435	179
Ni_2P/rGO/g-C_3N_4	10	300 W Xe lamp (λ > 420 nm)	10 vol% TEOA	2921	180
CdS@h-BN/rGO	10	Simulated solar light	10 vol% triethanolamine (TEA)	6465.33	181
P.RGO/MoS_2	2	400 W Xe lamp	20% (v/v) TEOA and 1 mL eosin Y	11 230	182
2D/2D MoS_2/g-C_3N_4-Au	200	300 W Xe lamp 420 nm cutoff filter	20 mL methanol	1100	183
Molybdenum sulfoselenide (MoSSe)@RGO	—	400 W Xe lamp (λ ≥ 420 nm)	Eosin Y and TEOA	5016	184
GQD/TpPa-1-COF	20	300 W Xe lamp	0.1 mol per L ascorbic acid	487	185
2D/2D Cu-tetrahydroxyquinone MOF (CuTHQ)/N-doped graphene (NG)	20	150 W Xe lamp	Methanol (MeOH)	164	186
Co-BDC MOF/GO	—	150 W halogen lamp	0.2 M TEOA and EY photosensitizer	14.5	187
2D/2D PRGO/CdS-diethylenetriamine (DETA)	50	0.35 M Na_2S, 0.25 M Na_2SO_3 and Pt cocatalyst	300 W Xe lamp with 400 nm cut-off filter	10 500	188
Cu_2O/RGO/$BiVO_4$	50	30 mL tetracycline	300 W Xe arc lamp (λ > 420 nm)	5.95	189
rGO-coupled C_3N_4/C_3N_5	50	10 vol% TEOA	300 W Xe lamp (λ ≥ 400 nm)	6380	190

electrodes, while Ag/AgCl acts as a reference electrode. As shown in Fig. 11b, n-type semiconductors have excess electrons and thus are used as photoanodes. Conversely, p-type semiconductors function as photocathodes due to their excess electron–hole pairs. Electrons are excited and move from the VB to the CB when the photoanode is exposed to light with an energy higher than its energy bandgap, followed by the movement of electrons toward the cathode to carry out a reduction reaction, while the holes left behind are involved in the process of oxidation.[200,201] With the need for an overpotential for each half-reaction, electrode resistance, loss from charge carriers' recombination, and potential decline at contacts, the energy required for PEC water splitting in practical systems can approach 2 V. To compensate for these losses and supply the energy needed for water splitting, an external bias is frequently used.[202] Fig. 11c illustrates the steps involved in the PEC water splitting mechanism for H_2 generation.

4.1.2. Overview of photocatalysts and 2D graphenes for green H_2 production. The overall water splitting involving the generation of H_2 and O_2 is an uphill process, requiring 1.23 eV energy. Therefore, the major prerequisite of a suitable catalyst is the band gap, which should be higher than 1.23 eV. Since 1972, after the exploration of water splitting by Honda and Fujishima, where a photoanode comprising TiO_2 and Pt cathode was used,[203] various catalysts including nitrides, oxides, sulfides, and carbides have been extensively explored for H_2 production *via* water splitting. The efficiency of all the explored catalysts is dependent on the solar light absorption ability, generation of charge carriers, separation of charge carriers, redox ability, more exposed surface area and stability. Moreover, the non-toxic nature and low cost are also the requirements for selecting a suitable catalyst for H_2 generation.[197,204–206]

Earlier, various semiconductor materials such as TiO_2,[207] $BiVO_4$,[208] WO_3,[209] perovskites,[210] g-C_3N_4,[211] LDHs,[212] ZrO_2,[213] and CdS[214] as photocatalysts have been researched for photocatalytic H_2 generation; however, they show poor efficiency towards photocatalytic H_2 generation mainly due to lower stability, wide band gap, and charge carrier recombination, whereas the photocatalysts having a narrow band gap suffer from a lower efficiency based on their surface area.[215] The utilization of metal-based photocatalysts is also explored extensively; however, metals are toxic and at the same time expensive.[216] In this regard, 2D materials as semiconductors for photocatalysis have attracted substantial attention as they offer excellent optical characteristics, good mechanical features, large surface area and less distance for the movement of electron–hole pairs to the solid–water interface.[217] Particularly, the heterojunction formation of 2D graphenes having a honeycomb structure with other semiconductor photocatalysts is considered to improve the overall photocatalytic H_2 production efficiency.[218] This is associated with the existence of an exceptional sp^2 hybrid C framework, making it highly conductive for thermal energy, *i.e.*, about 500 W m^{-1} K^{-1} and depicts an exceptional charge migration under ambient temperature condition, *i.e.*, about 200 000 cm^2 V^{-1} s^{-1}.[219] Besides, it shows a zero band gap and an enhanced surface area of about 2600 m^2 g^{-1}. Graphene-based

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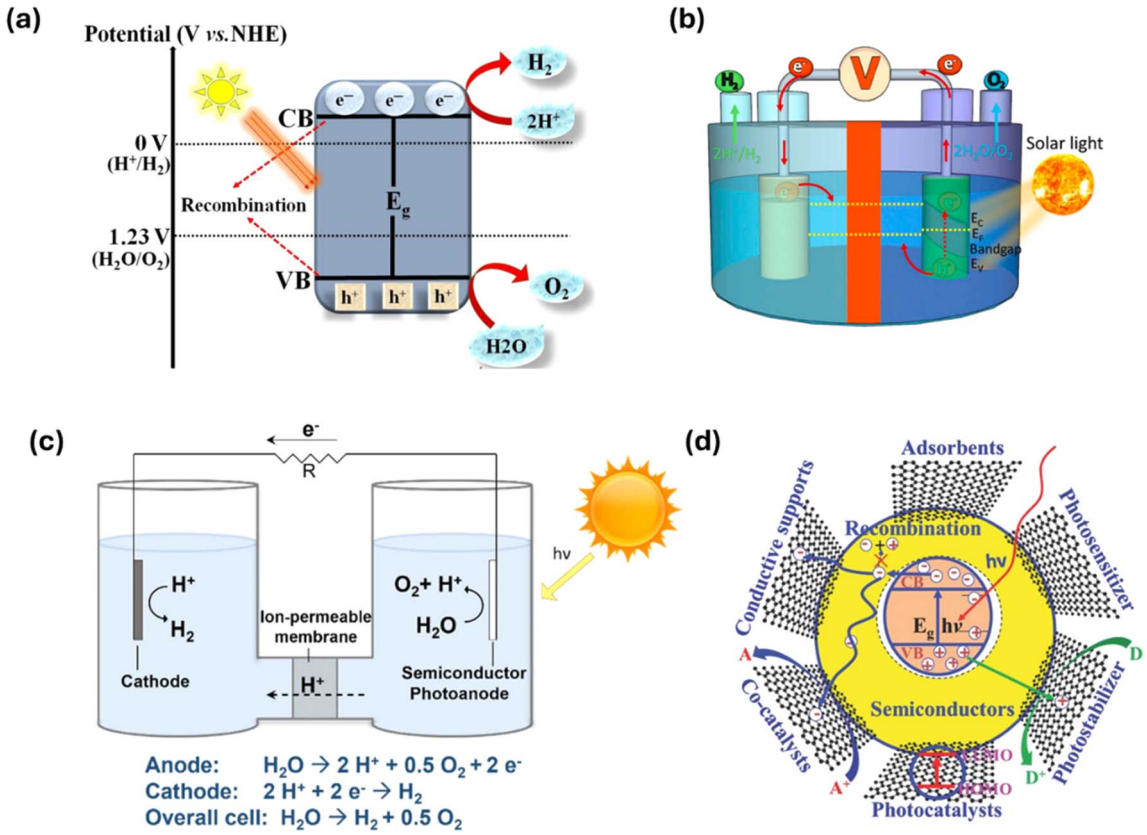

Fig. 11 (a) Illustrative overview of the general photocatalytic H_2 generation mechanism. (b) Representation of photoanodes and cathode semiconductors for PEC H_2 generation. (c) Mechanism of PEC water splitting for H_2 generation. (d) Characteristics of graphene for photocatalytic and PEC H_2 production.[197–199]

photocatalysts depict improved transfer and separation of electron–hole pairs.[220] Numerous published works used rGO as one of the standard semiconductor materials for improving the performance. RGO enhances the photocatalytic activity of these composites by facilitating the separation of electron–hole pairs across the catalyst/RGO contact. The photocatalytic H_2 production of the nanocomposites is largely dependent on the type of interface and defects present in the produced rGO.[221] rGO is unique as it possesses a variety of qualities that promote photocatalytic H_2 production efficiency. These properties include increased light utilization, charge carrier separation, intrinsic catalytic activity, and stability under operating conditions. While other photocatalysts could need co-catalysts or extra modifications to operate on par, their appropriateness varies depending on the demands of the given application and optimization techniques.[222] The efficient photocatalytic H_2 generation by graphene-based photocatalyst materials is due to the following mechanisms (Fig. 11d): (1) reduction of charge carrier recombination, (2) presence of catalytic active sites for reactions, (3) improved adsorption, (4) tunable band gap, and (5) potential to act as photosensitizers and cocatalysts.[59] Graphene derivatives including graphene oxide (GO) and reduced graphene oxide (rGO) contain epoxy, hydroxyl, and carboxyl surface groups having O_2, acting as catalytic reaction sites and also as supports for the uniform dispersion of metallic ions for nucleation and growth.[223] The dark colors of both GO and rGO lead to better absorption of light, expanding the absorption from the UV to the visible region.[224]

In the case of PEC H_2 production, photoelectrodes must possess the following features: (1) efficient absorption in the visible region, (2) appropriate band gap and positions for band edge to carry out redox reactions, and (3) stable nature in solutions of different pH values.[49] PEC H_2 production has been extensively studied for photocatalytic semiconductors such as TiO_2, MoS_2, WO_3, ZnO, α-Fe_2O_3, $BiVO_4$, Cu_2O, CdS, and Cu/Zn/W sulfide; however, certain challenges persist, leading to their poor PEC activity. For instance, TiO_2,[225] WO_3,[226] and ZnO[227] constitute wide band gaps and charge recombination, whereas α-Fe_2O_3 suffers from the demerits of short lifetime of charges, electron–hole pair recombination and less conductivity,[228] $BiVO_4$ also shows charge recombination[229] while Cu-based electrodes face the issue of photo corrosion, leading to less efficient PEC performance.[230] Lately, C-based materials such as graphene derivatives and rGO were studied to act as supports for developing different photoanodes due to their high surface area, excellent conductivity, charge movement, and stability.[231] Along with other semiconductor materials, they are known to show improved overall migration of charges, improve the photocurrent response and inhibit the process of photo corrosion.[232]

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Moreover, regarding heterojunction formation, 2D/2D heterostructures are known to depict excellent interface, leading to an improved surface area and less resistant electron transfer. Compared to the conventional interface, the 2D/2D interface provides a faster transport of charges which reduced their recombination.[233] Moreover, 2D/2D heterojunctions help in tuning the band edges for efficient redox reactions.[234] The heterojunction also leads to a stable heterostructure, less agglomeration and less photo-corrosion phenomena.[235]

4.1.3. Graphene-based 2D nanocomposites for photocatalytic hydrogen production. Regarding the utilization of graphene-based nanocomposites, due to the efficient electro movement in GO, MoS_2 were grown onto rGO followed by TiO_2 coupling. The H_2 production under UV light was 88 folds more than the H_2 production from pure TiO_2 because of the synergistic effect based on the ability of rGO towards efficient electron migration and MoS_2 acting as active sites.[176] The Ti_3C_2/TiO_2/rGO nanocomposite was studied for H_2 generation and the nanocomposite generated 808.11 μmol g^{-1} h^{-1} of H_2 within the 1st h, associated with the presence of the rutile phase of TiO_2 and rGO, which offered the pathway for the migration of electrons and minimized the recombination of charges.[236] A 2D carbon nitride (CN)@graphene@CN loaded with Pt was explored for photocatalytic H_2 generation, where under light irradiation, the electrons from the CB of CN were transferred to the graphene. The graphene aided in trapping the electrons and at the same time helped in their movement to the edges for their reaction with protons (Fig. 12a). The efficient activity was concluded to be dependent on the enhanced visible light absorption, excellent transfer of electrons across the interface, spatially divided redox active sites and the presence of excess active sites.[177] In another study, 2 wt% few-layer graphene (FLG)/graphitic carbon nitride (GCN) depicted 4-times 1274 μmol g^{-1} h^{-1} of H_2 under visible light, as shown in Fig. 12b and c along with an excellent stability over 4 consecutive cycles. As shown in Fig. 12d, electron–hole pairs were generated in CN, while the layered and 2D structure of CN aided in electron transfer from CN to FLG. FLG constitutes good electric conductivity, thus providing pathways for the movement of electrons, inhibiting electron–hole pair recombination. Moreover, the greater work function of the Pt metal enabled the transfer of electrons from FLG to Pt, for H_2 generation, while holes in GCN were quenched by the sacrificial agent.[178] Ni_2P/rGO/g-C_3N_4 was explored for efficient visible light-induced H_2 production and stability, which was associated with the active sites provided by Ni_2P and the synergistic effect of rGO towards the migration of electrons, leading to less charge recombination.[180] As shown in Fig. 12e, a solution-phase electrostatic assembly of polymer-functionalized rGO and boron carbon nitride (BCN) having positive and negative charges, respectively was used to synthesize polymer rGO (P.rGO) and polymer BCN (P.BCN). The 2D nanocomposite P.rGO/MoS_2 generated the highest yield of H_2 based on the presence of active sites for the reaction and improved the migration of charges within the layered structure.[182] In a current study, graphene quantum dots (GQDs)/TpPa-1-COF were studied for photocatalytic H_2 production, where the GQDs acted as photosensitizers for improving the light absorption and acted as a trap for electrons, leading to reduced recombination of electron–hole pairs. Moreover, the movement of electrons was aided due to the presence of an ohmic interaction among the covalent organic frameworks (COF) and GQDs.[185] In another work, the need for a noble metal as a cocatalyst was diminished while using 2D/2D Cu-tetrahydroxyquinone MOF (CuTHQ)/N-doped graphene (NG) nanocomposites for H_2 production. This was linked to the efficient migration of electrons between both photocatalysts, leading to less charge recombination. Therefore, the 2D/2D heterojunction helped in an increased yield of H_2 but at the same time played a vital role in separating electron–hole pairs, leading to noble metal-free photocatalytic H_2 generation.[186] Another noble metal-free photocatalytic H_2 generation was achieved by the fabrication of eosin Y (EY) dye-sensitized earth-abundant cobalt (Co-BDC) MOF with the addition of GO, where GO played a vital role as compared to EY in improving the H_2 generation under visible light irradiation. As shown in Fig. 12f, the irradiation is absorbed by the EY dye for the generation of singlet excited state, followed by quenching by TEOA or formation of ^{3}EY* and leading to quenching by amines for the generation of radical EY anions. Then, an electron migration from EY to GO occurs followed by migration to the MOF, which was considered the main reason for efficient H_2 generation.[187]

In conclusion, GO-based photocatalytic nanocomposites showed efficient and economic H_2 generation based on the improved surface area, migration of charges, separation of charges and provision of active sites. The incorporation of GO as a cocatalyst was explored to have the potential of replacing noble metals for photocatalytic H_2 generation. The 2D/2D GO/g-C_3N_4 heterojunction incorporated into other semiconductors was extensively studied for H_2 generation based on its simple fabrication, non-toxicity, efficient charge separation and transfer and active sites.

4.1.4. Graphene-based 2D nanocomposites for photoelectrochemical hydrogen production. LDHs are known to have a layered structure and good physio-chemical characteristics, but they are less conductive, have slow kinetics and are not stable in acids. The PEC H_2 production ability of the LDH was improved by forming 2D LDH@graphene and g-C_3N_4 heterojunction with MoS_2 as a co-catalyst (Fig. 12g). The heterojunction showed good production and stability for PEC H_2 production and also effectively separated the charges.[237] In another work, the MoS_2 was fabricated onto graphenes with Ag, which showed a photoconversion of 2.2% at −0.58 V for PEC water splitting. This is due to the plasmonic effect of Ag, leading to improved visible light absorption, and due to the heterojunction, which promoted charge segregation and migration. The Fermi level of pure graphene was positioned among the MoS_2 CB and the ITO, leading to electron withdrawal to the cathode, as indicated by Fig. 12h.[238] MoS_2/crumpled N-doped graphene p–n nanojunction was explored for PEC H_2 generation with an overpotential of approximately 100 mV *vs.* reversible hydrogen electrode (RHE). The N doped onto graphenes acted as support for the anchorage of MoS_2 and the presence of crumpled graphenes minimized the accumulation. Overall, the heterojunction helped in electron–hole pair separation.[239] Two-

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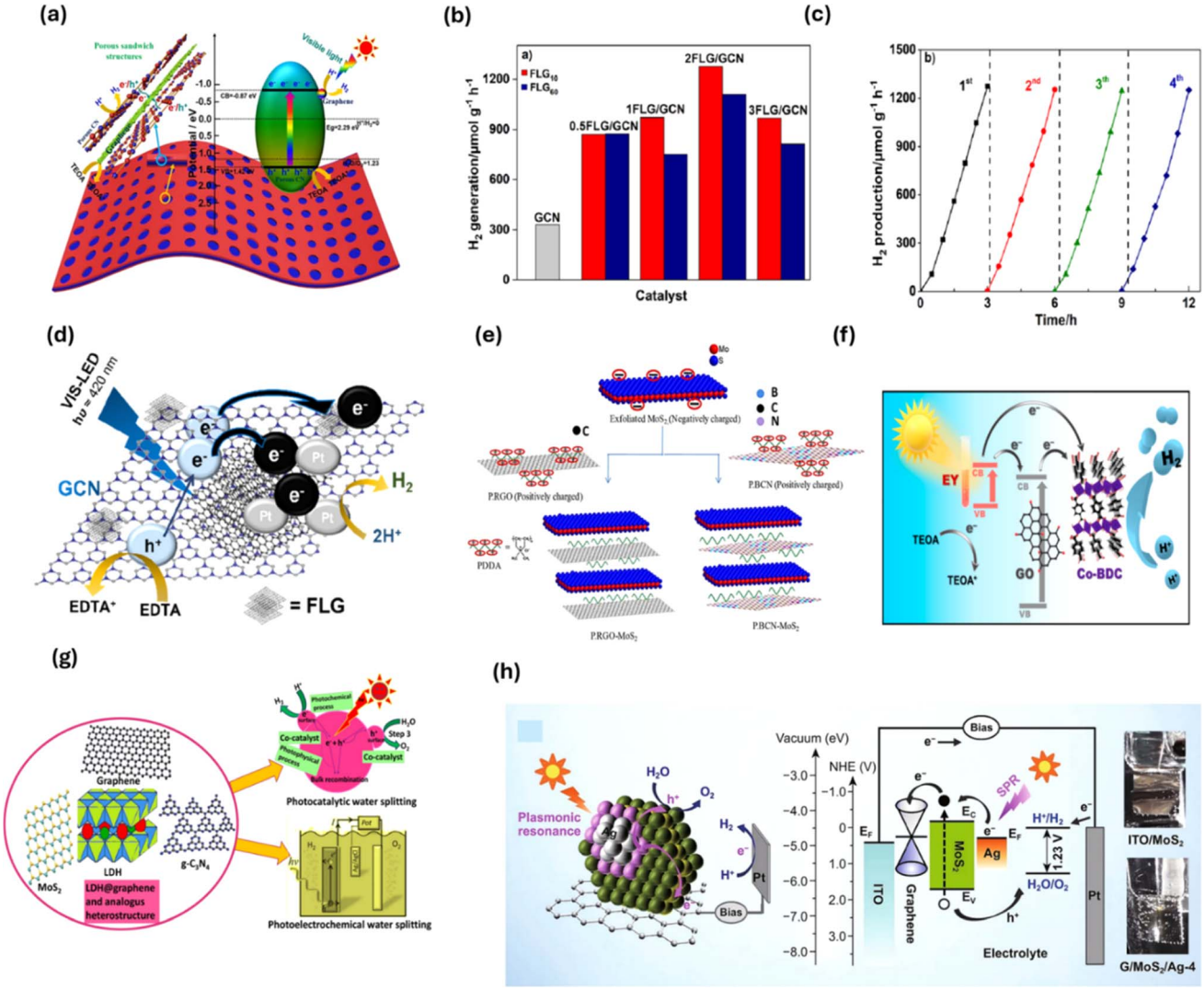

Fig. 12 (a) Illustrative overview of the charge transfer mechanism for the photocatalytic H_2 production process using 2D CN@graphene@CN loaded with Pt. (b) Rate of photocatalytic H_2 production and (c) stability over 4 consecutive cycles using FLG/GCN nanocomposites. (d) Charge transfer mechanism in the FLG/GCN nanocomposite. (e) Overview of the solution-phase electrostatic assembly to synthesize P.rGO and P.BCN. (f) Photocatalytic H_2 production mechanism in EY dye-sensitized Co-BDC MOF/GO. (g) Two-dimensional LDH@graphene and g-C_3N_4 heterojunctions for PEC H_2 generation. (h) Overview of the suitable Fermi level alignment and PEC H_2 generation in Ag-deposited MoS_2/GO.[177,178,182,187,237,238]

dimensional RGO wrapped in nanotubes of TiO_2 with decorated 2D MoS_2 was synthesized for H_2 generation, which was linked to the efficient charge transfer and the control on immobilized active sites.[240] A hybrid Ag@g-C_3N_4/r-GO nanocomposite was synthesized for PEC H_2 generation under visible irradiation. The nanocomposite showed durability, efficient activity and adaptability for PEC reaction. An apparent quantum yield of 1.69 and a rate of 954 μmol g^{-1} h^{-1} for photocatalytic H_2 generation were achieved in the presence of simulated solar light while an overpotential value of 0.484 V at a current density of 10 mA cm^{-2} was achieved in PEC H_2 generation activity.[241] In another study, a graphene/WS_2 nanocomposite was explored as a photoanode for PEC H_2 generation. The nanocomposite depicted an efficient absorption of 98% under visible irradiations. The increased visible light absorption resulted in excellent generation of electrons with improved movement of charges.[242]

In conclusion, the literature to date has shown that adding graphenes at certain interfaces can improve the PEC efficiency of photoelectrodes towards PEC H_2 generation. The high electric conductivity of graphenes, which enhances the charge carrier movement across the heterojunction components, is responsible for the significant increases in the efficiency; however, in literature for PEC H_2 production using 2D/2D graphene and its derivatives.

4.2 Hydrogen storage using graphene-based nanomaterials

Graphene-based 2D nanomaterials are found to be promising candidates for practical solid-state hydrogen storage applications due to their exceptionally large surface area (2600 m^2

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Table 2 Hydrogen storage using various graphene-based nanomaterials

Material	Pressure (bar)	Temperature (K)	Hydrogen storage (wt%)	Reference
Graphene nanosheets	100	298	0.9–1.5	244 and 245
	10	77	1.2	
Hierarchical graphene	1	77	4.0	246
Graphene oxide	50	298	1.4	247
Functionalized graphene with $ClSO_3H$	2	77	1.6	248
Functionalized graphene with oleum	2	77	1.4	
Functionalized graphene with Pt nanoparticles	57	303	0.15	249
Functionalized graphene with Pd nanoparticles	40	298	0.81	250
N-doped graphene	90	298	1.5	251
Li-decorated N-doped penta graphene	—	—	7.88	252
Pd_3Co-decorated nitrogen/boron-doped graphene	30	298	4.6	253
Phosphorous doped graphene	100	—	2.4	251
Li-decorated holey graphyne	—	—	12.8 (simulation result)	254
Lithium decorated ψ-graphene	—	—	15.15 (simulation result)	255
Ti doped ψ-graphene	—	—	13.14 (simulation result)	256
Zr decorated ψ-graphene	—	—	11.3 (simulation result)	257
Zr-decorated γ-graphyne monolayer	—	—	7.95 (simulation result)	258
Nitrogenated holey graphene (C_2N) with titanium clusters	—	—	6.8	259
3D-graphene	1	77	1.4	260
Transition metal-decorated boron doped twin-graphene	1	77	4.95	261
Lithium doped fullerene pillared graphene nanocomposites (Li-FPGNs)	—	—	9.1	262
Ni/Pd co-modified graphene	4	298	2.65	263
Gold decorated graphene nanosheet	—	—	4.65	264
Diatom frustule-graphene	20	298	4.83	265
Fe–Ti decorated defective graphene	—	—	5.1	266
Ca on graphene	—	—	5–6	
$Mg_{2.3}Y_{0.1}Ni$ alloy with graphene	—	—	3.25	267

g^{-1}), porous structure, and high chemical and thermal stabilities.[243] Pristine graphenes generally have low hydrogen storage capacities while functionalizing graphene nanosheets drastically improve their performance.[244,245] The functionalization includes doping with hetero atoms such as boron (B) and nitrogen (N), decorating with metal atoms, and defect engineering in the nanosheets (Table 2). Moreover, the graphene nanosheets allow surface curvature tuning, which would help develop a reversible hydrogen storage system with enhanced kinetics.[60]

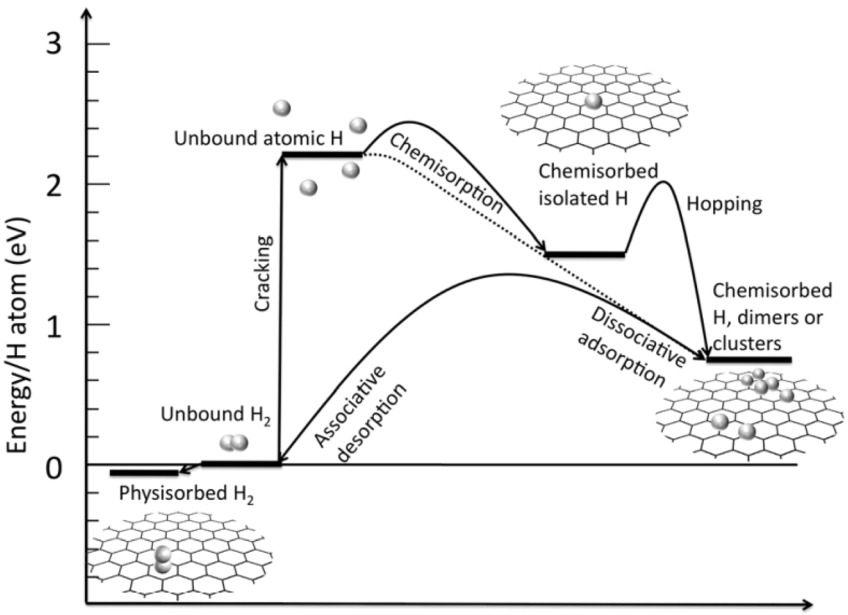

Fig. 13 Energy level diagram of hydrogen adsorption–desorption on the graphene monolayer.[60] Adapted with permission from RSC.

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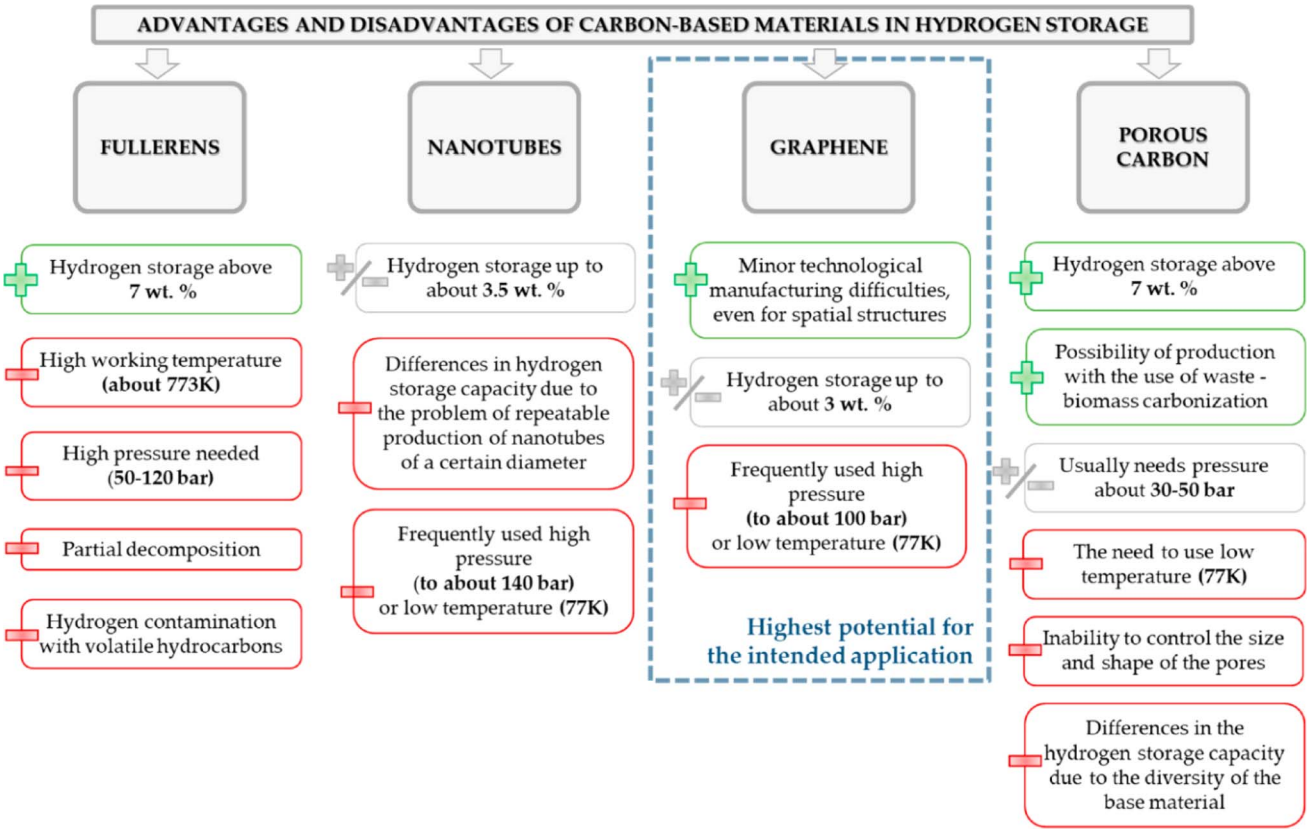

Fig. 14 Summary of solid-state hydrogen storage using different carbon-based materials.[244] Adapted with permission from MDPI.

The adsorption of hydrogen molecules onto graphene sheets can occur either by physisorption (van der Waals interactions) or by chemisorption (chemical bonds with carbon atoms). The theoretical energy requirement for the physisorption of hydrogen molecules (H_2) on single-layer graphenes was evaluated to be in the range of 0.01–0.06 eV (Fig. 13). Even though the energy requirement for hydrogen adsorption onto the graphene sheet is quite low, it still requires low temperatures and high

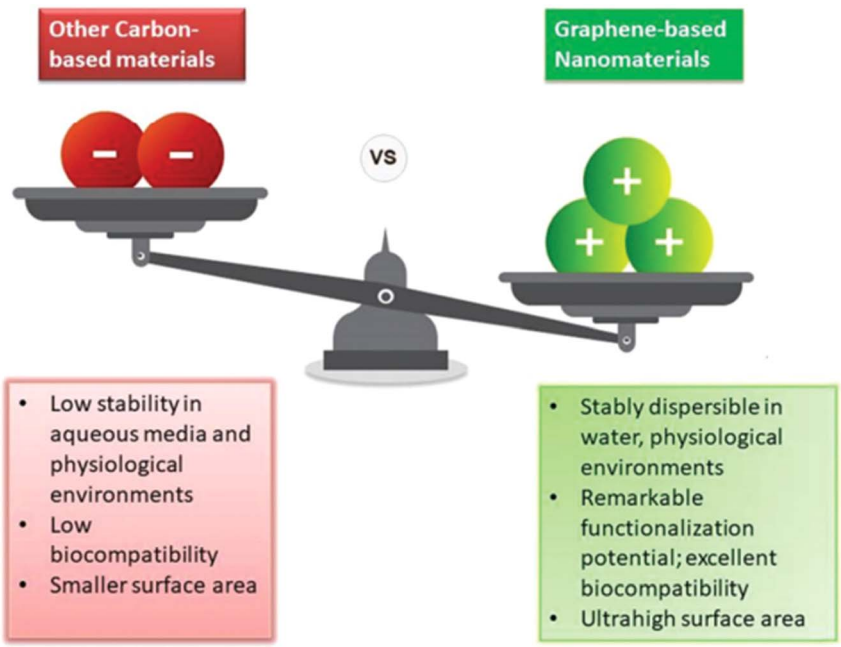

Fig. 15 Advantages of the graphene nanomaterial over other carbon-based nanomaterials. Adapted with permission from RSC.[268]

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pressures to achieve reasonable hydrogen storage capacities. Chemisorption requires the dissociation of hydrogen molecules, and consequently, the energy requirement is much higher (1.5 eV) (Fig. 13) than that of physisorption. Hydrogen storage capacities of various graphene-based 2D nanomaterials are summarized in Table 2.

A significant progress has been made in the field of hydrogen storage using graphene-based 2D materials. Among various graphene-based 2D nanomaterials, alkali, alkaline earth, and transition metal nanoparticle-decorated graphene doped with hetero atoms are found to be potential candidates for this purpose. In addition, the functionalized graphene nanosheets are distinctly advantageous than other carbon allotropes such as fullerene, nanotubes, and porous carbons, as shown in Fig. 14. Nevertheless, the adsorption and desorption properties of hydrogen molecules in 2D nanomaterials are still unclear. Therefore, hydrogen storage at ambient temperatures and pressures using functionalized graphene nanosheets even remains a challenge.

5. Summary and outlook

As society's energy needs increase, lithium batteries for energy storage require efficient electrode materials to store energy and the ability to be charged more quickly. Moreover, hydrogen, with the current rate of industrialization leading to greenhouse gas (GHG) emissions, is considered a potential energy carrier that can replace fossil fuels. However, the materials for hydrogen production and storage show challenges of inefficiency and cost-effectiveness. The development of 2D materials may offer a solution to these issues. Graphene is a two-dimensional substance that exhibits remarkable mechanical strength, exceptional conductivity, superb flexibility, high surface area and excellent chemical stability. With these properties, graphenes are desirable for energy storage, hydrogen production and electronic applications (Fig. 15). The synergistic effect of graphenes with 2D composite materials is appropriate for fabricating electrodes of lithium batteries because of their high interlayer adsorption energy and a large specific surface area. As graphenes and 2D composite materials have special features, they can be employed to create stable SEI layers, serve as anode hosts, alter the separator interface (LSB), and change the electrolyte (manage the polysulfides). Additionally, graphenes can enhance the electrical conductivity of two-dimensional materials and lessen volume fluctuations. Apart from this, in terms of H_2 production, GO-based photocatalytic nanocomposites show efficient and economic H_2 generation based on the improved surface area, efficient migration of charges, separation of charges, and provision of active sites. Moreover, in the case of PEC H_2 generation, graphenes show high electric conductivity for efficient charge carrier movement.

Data availability

The data that support the findings of this study are available from the corresponding author.

Conflicts of interest

The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

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