Strategies for improving the lithium-storage performance of 2D nanomaterials

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ABSTRACT

2D nanomaterials, including graphene, transition metal oxide (TMO) nanosheets, transition metal dichalcogenide (TMD) nanosheets, etc., have offered an appealing and unprecedented opportunity for the development of high-performance electrode materials for lithium-ion batteries (LIBs). Although significant progress has been made on 2D nanomaterials for LIB applications in recent years, some major challenges still exist for the direct use of these sheet-like nanomaterials, such as their serious self-agglomerating tendency during electrode fabrication and low conductivity as well as the large volume changes over repeated charging–discharging cycles for most TMOs/TMDs, which have resulted in large irreversible capacity, low initial Coulombic efficiency and fast capacity fading. To address these issues, considerable progress has been made in the exploitation of 2D nanosheets for enhanced lithium storage. In this review, we intend to summarize the recent progress on the strategies for enhancing the lithium-storage performance of 2D nanomaterials, including hybridization with conductive materials, surface/edge functionalization and structural optimization. These strategies for manipulating the structures and properties of 2D nanomaterials are expected to meet the grand challenges for advanced nanomaterials in clean energy applications and thus provide access to exciting materials for achieving high-performance next-generation energy-storage devices.

Keywords: 2D nanomaterials, lithium-ion batteries, graphene, energy-storage devices

INTRODUCTION

Electrochemical energy-storage (EES) systems, including capacitors and batteries, have been extensively applied in a wide range of fields, such as electric vehicles (EVs), smart electrical grids and numerous portable electronic devices, and help address the challenges arising from global climate change and the progressive shift of energy production from traditional fossil fuels towards renewable energy sources. Among the various types of EES systems, Li-ion batteries (LIBs) have become the major power supplies for portable electronics and EVs, because of their high specific energy density, low self-discharge and low memory effect [1,2]. The performance of the current LIBs, however, is still not satisfactory to meet the ever-growing demands for batteries. To achieve long-lifetime and long-distance power supplies, LIBs are urgently required to be innovated in terms of higher energy density, lighter weight, longer lifespan, lower cost and improved safety [3–5]. Most of these concerns are related to electrode materials, which play a key role in enhancing the electrochemical properties of batteries [6–8]. Thus, the discovery of advanced electrode materials for high-performance LIBs with improved lithium-storage properties has been the major objective of research to lead to much more widespread applications of this promising class of EES devices.

2D nanomaterials—a class of materials composed of one or several monolayers of atoms (or unit cells)—have attracted intensive interest in recent years, due to their outstanding physical and chemical properties arising from their unique morphology in contrast to their bulk counterparts, such as fascinating chemical activities, excellent mechanical strength, extremely large specific surface area, etc. [9–18]. It has been demonstrated that the integration of 2D nanomaterials with clean...
energy devices offers promising opportunities to address the major challenges driven by ever-growing global energy demands [19,20]. Following the most studied graphene, various graphene-like nanomaterials have recently been discovered, including borophene [21,22], silicene [23], germanene [24], arsenene [25], stanene [26], antimonene [27], phosphorene [28–30], hexagonal boron nitride [31], carbon nitride [32], metal oxide nanosheets [33], metal sulfide nanosheets [34–38], metal hydroxide nanosheets [39], 2D covalent-organic frameworks (COFs) [40], 2D metal-organic frameworks (MOFs) [41–44], MXene [45,46], etc. Among these, graphene, transition metal oxide (TMO) nanosheets and transition metal dichalcogenide (TMD) nanosheets are three representative types of 2D nanomaterials, which have been extensively explored as promising electrode materials for LIBs [47–61]. The popular graphene features super-high theoretical surface area (~2630 m²·g⁻¹) and exceptional room-temperature electron mobility (~2.5 × 10⁶ cm²V⁻¹s⁻¹), which allows large interfacial lithium storage and fast charge/carrier transport, while most TMOs (e.g. VOₓ, CoOₓ, MnOₓ, FeOₓ, NiOₓ, MoOₓ, TiOₓ, etc., and their hybrids) and TMDs (e.g. MoS₂, WS₂, CoS₂, NiS₂, etc.) offer outstanding ion transport kinetics and chemically active interfaces, and thus have superior storage performance [62–73]. Besides the progress on novel 2D nanomaterials achieved by experimentalists, some systematical theoretical predictions have proved that reducing the dimensionality of nanomaterials to 2D from their corresponding bulk could effectively decrease the binding energy and the diffusion barrier of Li or other alkali metal ions, and hence enhance the ion mobility [74–76]. It has been theoretically demonstrated that the Li mobility in MoS₂ bilayers and monolayers can be increased by a factors 10² and 10⁴, respectively, compared to that in bulk MoS₂ at room temperature [74], and some 2D nanomaterials show a higher theoretical capacity and/or a higher stable specific capacity at high current density during long cycling than the corresponding bulk inorganic crystal anodes [75].

Despite their significant advantages for LIBs, the direct use of 2D nanomaterials has met with numerous challenges. First, the surfaces of 2D nanosheets, particularly pristine graphene, present inferior chemical affinity to other component materials in practical applications, which results in poor interface compatibility, low electric/ionic conductivity, long electron/ion diffusion paths and slow chemical reactivity. Compared to 3D nanostructures, the number of active sites for anchoring lithium ions on the surface of the 2D sheet-like planes is relatively limited. Second, while 2D nanomaterials have a high theoretical specific surface area, the surface of 2D nanosheets is by no means completely available due to restacking or aggregation of the primary sheets during materials processing or device fabrication steps. Third, the intrinsic low conductivity of most TMOs and TMDs and the large volume changes over repeated charging-discharging cycles lead to large irreversible capacity, low initial Coulombic efficiency and fast capacity fading. To deal with these challenges for the application of 2D nanomaterials in LIBs, some strategies, such as surface functionalization, strongly coupled inorganic nano-graphene hybridization, defect engineering, etc., have been proven to be effective approaches for the enhancement of the electrical conductivity or the ion transport during electrochemical reactions, thus leading to improved rate capability and cycling stability as electrode materials for LIBs.

In this review, we summarize the recent progress and classify it into three primary strategies for enhancing the lithium-storage performance of 2D nanomaterials for LIBs. These strategies include hybridization with conductive substrates, edge/surface functionalization and structure optimization (Fig. 1). The strategy of hybridization is the most common and widely studied one for TMOs/TMDs-based nanocomposites, in which some conductive nanostructures, e.g. nano-carbon, carbon nanotubes (CNTs), graphene, organic polymers, metallic nanoparticles, etc., are introduced to hybridize with TMO/TMD nanosheets to improve the overall conductivity and accommodate the volume expansion of metal oxide or sulfide nanomaterials during the repeated charging/discharging cycles. The second strategy is edge/surface functionalization, which can be achieved by atom/ion doping or defect engineering at the edges or on the surfaces of the 2D nanomaterials. The implantation of heteratoms or ions into 2D nanomaterials helps to modulate the electronic structure, the surface chemical reactivity, or the interlayer spacing of the 2D nanomaterials, and further enhances the lithium-ions storage capacity. The third strategy of structure optimization is often realized by controlling some structural parameters during fabrication, such as thickness, size, pores or surface morphology, which have significant impacts on the structure-dependent properties and the electrochemical performance, and are beneficial for alleviating the inevitable self-restacking and exposing more active sites. Hence, these strategies for manipulating the structures and properties of 2D nanomaterials are effective for overcoming the key challenges obstructing the use of advanced materials in clean energy applications and thus provide exciting materials for achieving
Strategies for improving lithium storage properties of 2D nanosheets

Figure 1. Schematic illustration of the pathways for lithium-ion diffusion and transfer (top) and the strategies for improving the lithium-storage properties of 2D nanosheets (bottom).

high-performance next-generation energy-storage devices.

STRATEGY 1: HYBRIDIZING TO FORM 2D HYBRID NANOMATERIALS

Hybridizing property-complementary nanomaterials into multifunctional nanocomposites that exhibit good synergistic effects in combination with the merits of each constituent is one of the mostly widely used strategies for improving the electrochemical properties of 2D nanomaterials, especially for the hybridization between TMO or TMD nanosheets and some conductive nanostructures. It has been reported that the outstanding properties of 2D nanomaterials in their pristine forms are nevertheless insufficient to satisfy the increasing demands for LIB applications. Pristine graphene, which has exceptional electron mobility, for example, is only chemically active at the edges, but not on the surfaces, and cannot provide a stable potential output [77], while TMOs and TMDs are intrinsically inferior in terms of electric conductivity. Many 2D TMO or TMD nanosheets have been reported to hybridize with some property-complementary conductive nanomaterials, including graphene, carbon, CNTs, organic polymer and metallic nanoparticles. Via this technique, the overall electrical conductivity can be greatly enhanced, contributing to the reduction of interior resistance and the acceleration of the electrochemical reaction rate. At the same time, the obvious volume changes of TMO or TMD nanoparticles caused by repeated intercalation/de-intercalation can be also effectively alleviated without unexpected pulverization after a considerable number of cycles. In this section, five typical types of hybrid structures between the TMO or TMD nanosheets and conductive nanostructures, such as 2D nanomaterials hybridized with graphene, 2D nanomaterials hybridized with nano-carbon, 2D nanomaterials hybridized with CNTs, 2D nanomaterials hybridized with conductive polymers and 2D nanomaterials hybridized with metallic nanoparticles, are summarized.

2D nanomaterials hybridized with graphene

Graphene is one of the most studied substrate materials for hybrid nanomaterials, which has been well documented in many excellent review papers [78–87]. In this work, owing to the limited space, only the 2D-2D hybrid nanocomposites between TMO or TMD nanosheets and graphene are discussed. Various TMO or TMD nanosheets have been used to integrate with graphene to form graphene-based composites, including MoS2 [88–92], WS2 [93,94], TiO2 [95,96], Cr2O3 [97], Fe2O3 [98], Co3O4 [99,100], SnOx [101], NiCo2O4 [102], ZnMn2O4 [103], CoO [104], etc. The hybridization of these 2D nanomaterials with graphene can be divided into three types: horizontal growth of 2D nanostructures on the graphene surface, vertical growth of 2D nanostructures on graphene surfaces and layer-on-layer sandwiched 2D-graphene nanostructures. In these three types of configurations, the horizontal growth can enhance the binding between the nanosheets and the graphene, while the vertical growth provides more active sites for ion transport and more open spaces for volume change accommodation, and the layer-on-layer or sheet-on-sheet sandwiched structures can achieve the maximum utilization of the merits of the 2D sheet-like nanomaterials without evident aggregation, provide better buffering ability for volume expansion and contraction, and strengthen the electrode with good flexibility and remarkable adhesion. Figure 2 presents typical examples of
the TMO or TMDs nanosheets hybridized with graphene and their electrochemical properties as electrode materials for LIBs.

In comparison with other graphene-based nanocomposites, such as nanowires deposited on graphene and nanospheres encapsulated by graphene, the horizontal growth of layered TMO or TMD nanosheets on the surface of graphene to form 2D-2D hybrid structures has significant geometrical compatibility and increases the possibility of forming stronger interactions, and thus leads to favorable rate capability and cycling stability. As shown in Fig. 2a, well-dispersed, flat, leaf-like composites of nitrogen-doped graphene (NG) integrated with few-layer WS2 have been synthesized by Chen et al. using a surfactant-assisted hydrothermal synthesis [93], where the TMD precursor was reduced and assembled with nitrogenized reduced-graphene oxide (rGO) formed in situ in the presence of cetyltrimethyl ammonium bromide.

Figure 2. 2D nanomaterials hybridized with graphene. (a) Nitrogen-doped graphene (NG) integrated with few-layer WS2 nanosheets (WS2–NG) [93] (Copyright 2013, The Royal Society of Chemistry); (b) MoS2 nanosheets (NSs) vertically grown on graphene sheets (MoS2/G) [90] (Copyright 2016, American Chemical Society); (c) sandwich-like mesoporous TiO2/graphene/mesoporousTiO2 hybridnanosheets (G@mesoporousTiO2 nanosheet) [96] (Copyright 2015, American Chemical Society); (d) atomically thin mesoporous Co3O4 nanosheet hybrid with graphene (ATMCNs-GE) [99]; (e) cycling performance and Coulombic efficiency of ATMCNs-GE hybrid nanomaterials at a current density of 2.25 C [99] (Copyright 2016, Wiley-VCH).
(CTAB) surfactant. Electrochemical measurements confirmed that there was only 0.08% capacity fade per cycle for 100 cycles and 80% capacity retention after a dramatic increase in current density from 0.1 A g$^{-1}$ to 5 A g$^{-1}$ with a voltage window between 0 and 3.0 V [93].

Figure 2b shows the perpendicular growth of vertical MoS$_2$ nanosheets (NSs) on graphene sheets (MoS$_2$/G) by using Mo$_7$O$_{24}^6$− and thiocarbamide (CH$_3$CSNH$_2$) as S and Mo sources, respectively [90]. In this unique structure, the vertically grown MoS$_2$ nanosheets offer an increased number of active sites and open channels for the intercalation of lithium ions, while the graphene provides high-speed electron-transfer pathways and a flexible substrate for buffering volume changes over lithiation/delithiation cycles. When used as the anode material for LIBs, the MoS$_2$/G composite reached a capacity of 1077 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ after 150 cycles and still retained 907 mA h g$^{-1}$ at 1.0 A g$^{-1}$ over 400 cycles [90].

The sandwiched or layered nanostructures of TMO or TMD nanosheets with graphene have great potential for lithium-ion storage. The presence of graphene between the layers of TMO or TMD nanosheets could prevent the restacking of nanosheets and significantly improve the conductivity of the whole electrode, which is favorable for charge transfer during the electrochemical reactions. Liu et al. reported a simple and general filtration vacuum technique to directly assemble flexible lamellar WS$_2$/reduced-graphene oxide composite (WS$_2$/rGO) papers. The WS$_2$/rGO had a high reversible capacity of 697.7 mA h g$^{-1}$ as binder-free anode for LIBs at a current density of 100 mA g$^{-1}$ after 100 cycles, which is over eight times higher than the 88.5 mA h g$^{-1}$ for pure WS$_2$ nanosheets [94]. Yang et al. developed a nanocasting strategy for the synthesis of graphene-TiO$_2$ hybrid (G-TiO$_2$) nanosheets with graphene-based silica nanosheets (G-silica) as a sacrificial template [95]. In this synthesis, G-silica nanosheets were first prepared via the hydrolysis of tetraethylorthosilicate on the surface of graphene oxide, followed by pyrolysis to transform the precursor into graphene-silica nanosheets (GO-silica). Sandwich-like graphene-based mesoporous TiO$_2$ nanosheets with a thickness of 50 nm were then obtained by a sol-gel process from the GO-silica in a solution of (NH$_4$)$_2$TiF$_6$ and H$_2$BO$_3$ at 50°C, and then the silica layer was removed by etching in a NaOH solution. This as-obtained sandwich-like textured nanostructure have many unique advantages to facilitate the insertion/deinsertion of Li ions, such as ultrathin thickness, mesoporous structure, high surface area and uniform dispersion of the graphene layers in between the TiO$_2$ nanosheets. Remarkably, the reversible capacities of these sandwiched nanosheets were 162 and 123 mA h g$^{-1}$ at 1 C and 10 C, respectively [95].

In the traditional fabrication of graphene-based hybrid materials, the TMO nanosheets often only grow at the defect sites of the graphene surfaces and form discontinuous island-like domain arrays. Li et al. synthesized uniform mesoporous TiO$_2$/graphene/mesoporous TiO$_2$ sandwich-like nanosheets (G@mTiO$_2$) by slow hydrolysis and condensation of Ti precursor (tetrabutyl titanate, TBOT) on graphene sheets in an ammonia solution with a following heating treatment at 500°C in argon (Fig. 2c) [96]. These nanosheets with the formation of a continuous and conformable coverage shell on graphene demonstrated an ultrathin thickness of ∼34 nm, a planar size in the range of ∼1-20 μm, well-crystallized constituent nanocrystals ∼6 nm in size, a high specific surface area of ∼252 m$^2$g$^{-1}$ and well-distributed mesopores ∼3.4 nm in size. This hybrid nanomaterial featured high contact area between graphene and TiO$_2$ nanocrystals and allowed more effective usage of the graphene surface for electron transfer and the interfaces for lithium storage. When applied as an anode for LIBs, it gave a reversible capacity of 237 mA h g$^{-1}$ after 100 cycles at a current density of 20 mA g$^{-1}$ [96].

Recently, atomic layer-by-layer Co$_3$O$_4$/graphene (ATMCNs-GE) hybrid nanomaterial has been fabricated as anode materials for LIBs by Dou et al. via a surfactant-assisted self-assembly method together with a following calcination process, as shown in Fig. 2d [99]. The as-prepared Co$_3$O$_4$ nanosheets with numerous mesopores on the surface possessed a thickness of ∼2.0 nm, a lateral size of about 2.5 μm and a surface area of ∼157 m$^2$g$^{-1}$. When utilized as anode for LIBs, this hybrid nanomaterial delivered high discharge capacities of 2014.7 and 1134.4 mA h g$^{-1}$ at 0.11 C and 2.25 C (1 C = 890 mA h$^{-1}$), respectively. Even more attractive, as demonstrated in Fig. 2e, 92.1% of the original capacity remained after 2000 cycles at a rate of 2.25 C, suggesting exceptional cycling stability compared to other Co$_3$O$_4$/C composites [99]. The outstanding electrochemical performance of the ATMCNs-GE hybrid nanomaterial was mainly attributable to the unique structure: the atom-level thickness and the mesoporous structure of the Co$_3$O$_4$ nanosheets allowed adequate electrode/electrolyte contact and shortened the Li$^+$ diffusion length, while the graphene substrate with high electrical conductivity and excellent flexibility improved the electronic/ionic transportation and enhanced the structural stability.
It is noteworthy that the formation of new bonds between the hybrid nanosheets contributes to preventing structural damage from massive lithium-ion intercalation and facilitates the electron transport, and thus improves the structural stability and electrochemical performance of the electrodes. Dou et al. stated that the formation of C-O-Co bonds between the graphene and the Co3O4 nanosheets contributed to the high-performance of the ATMCNs-GE hybrid nanomaterials [99]. Zhou et al. have also demonstrated the presence of oxygen bridges (C-O-Ni linkage) between graphene and NiO nanosheets (NiO NSs), which could result in close interfacial interaction in the 2D sheet-on-sheet graphene-metal oxide nanocomposites and might be the origin of the synergistic effect behind their significantly enhanced electrochemical performance [105]. Electrochemical experiments demonstrated that the composites with NiO NSs and graphene delivered a high initial reversible capacity of 1000 mA h g⁻¹—much larger than for a NiO NS–graphene mixture (696 mA h g⁻¹) and NiO NSs (602 mA h g⁻¹). This value was obviously higher than the total theoretical capacity of the composites (709 mA h g⁻¹), which was calculated based on the mass fraction of the two components and the individual capacities of NiO NSs (602 mA h g⁻¹) and graphene (1091 mA h g⁻¹). The as-obtained nanocomposites also presented a stable reversible capacity of 883 mA h g⁻¹ over 50 cycles at a current density of 50 mA g⁻¹—much better than that of the NiO NS–graphene mixture (530 mA h g⁻¹) and NiO NSs (210 mA h g⁻¹) [105].

In summary, the hybridization of TMO or TMD nanosheets with graphene via in-situ chemical growth or direct physical mixing has demonstrated a bright future for LIB anodes. The primary functions of graphene in this family of hybrid nanomaterials can be summarized as follows: (i) increasing electrical conductivity to facilitate electron transport within the electrode; (ii) accommodating volume expansion during cycling and thus avoiding the rapid pulverization and even cracking of the electrode; (iii) maintaining the good dispersion of the nanosheets and preventing the agglomeration of 2D TMD/TMO nanomaterials; and (iv) offering high specific surface areas to act as active sites for anchoring lithium ions. Some major challenges, however, still remain, such as the difficulty in assembling hybrid nanomaterials with predetermined or precisely controlled stacking layers, the weak contact between the TMDs/TMOs and graphene, and the inhomogeneous distribution of TMDs/TMOs on graphene nanosheets, which require further extensive efforts on this class of interesting materials.

2D nanomaterials hybridized with nano-carbon materials

Unlike graphene, nano-carbon materials have various morphologies, including nanofibers, nanosheets, nanoboxes, etc., which offer the possibility of forming nano-carbon and TMO/TMD nanosheet hybrid materials in miscellaneous shapes and dimensions. Moreover, the coating or deposition of nano-carbon on 2D TMO/TMD nanosheets or vice-versa is much simpler and easier compare to graphene-based hybrid nanomaterials. Figure 3 illustrates five typical 2D TMO/TMD-nano-carbon hybrid nanostructures, including nanosheets coated with amorphous carbon (Fig. 3a) [106], nanosheets on ordered mesoporous carbon (Fig. 3b) [107], nanosheets-on-carbon nanoboxes (Fig. 3c) [108], nanosheets-on-carbon nanofibers (Fig. 3d) [109] and nanosheets-on-carbon nanosheets (Fig. 3e) [110,111]. These hybrid nanomaterials are effective for preventing the self-restacking of 2D nanosheets, improving the conductivity, accommodating the volume changes and decreasing pulverization of the electrodes.

Xu et al. have fabricated carbon-coated troilite FeS (C@FeS) nanosheet hybrid materials by using 1-dodecanethiol (DDT) as sulfur source and surfactant, in which the iron and sulfur atoms react to form thin layers of FeS, while the hydrocarbon tails of 1-dodecanethiol separate the thin FeS layers, which turn to carbon after annealing in Ar atmosphere (Fig. 3a) [106]. The amorphous carbon-coated FeS polycrystalline nanosheets, after annealing at 400°C for 2 h, presented a thickness ranging from 4 to 10 nm, a lateral size between 100 and 200 nm, and an estimated specific surface area of 80.9 m² g⁻¹. When evaluated as electrode material for LIBs, the C@FeS nanosheets demonstrated an excellent ninth cycle specific discharge capacity of 266 mA h g⁻¹ at a high current density of 6 A g⁻¹. Moreover, the C@FeS nanosheets delivered a remarkable capacity of 615 mA h g⁻¹ over 100 cycles at a rate of 0.1 A g⁻¹ in the voltage range of 0.01–3.0 V, which was higher than for C@FeS nanospheres (580 mA h g⁻¹) and C@FeS nanoplates (525 mA h g⁻¹) [106].

Highly ordered carbon mesoporous structures, such as CMK-3, which displays highly ordered, uniform and interconnected porous channels, uniform carbon walls and large pore volume, have been employed as outstanding conductive substrates to hybridize with 2D metal oxides or sulfides. Figure 3b presents a NiO nanosheets-CMK-3 mesoporous carbon hybrid material developed by Fan et al., in which ultrathin NiO nanosheets (NiO NSs) were anchored on CMK-3 [107]. In this hybrid nanostructure, the NiO NSs had an ultrathin thickness...
of 4.9 nm, and the CMK-3 fibers presented highly ordered, unblocked and mesoporous channels, giving the composite a super-high specific surface area of 734 m$^2$/g—much larger than that for NiO NSs ($\sim$200 m$^2$/g). In this hybrid material, the ultrathin porous NiO nanosheets and the interconnected carbon nanowalls shortened the diffusion paths for Li$^+$ and allowed rapid electron transfer and Li$^+$ diffusion. The obtained composite delivered an excellent rate performance (824 mAh g$^{-1}$ at a current density of 800 mA g$^{-1}$), a high reversible specific capacity (940 mAh g$^{-1}$ at the second cycle at 400 mA g$^{-1}$) and good cycling stability (847 mA h g$^{-1}$ over 50 cycles at 400 mA g$^{-1}$) compared to the aggregated NiO NSs (148 mA h g$^{-1}$ over 50 cycles at 400 mA g$^{-1}$) and bare CMK-3 ($\sim$450 mAh g$^{-1}$ over 50 cycles at 400 mA g$^{-1}$) [107].

Figure 3c shows a nanosheets-on-carbon nanobox hybrid structure (C@MoS$_2$) designed by Yu et al. by growing ultrathin MoS$_2$ nanosheets on the surfaces of N-doped carbon nanoboxes, in which uniform $\alpha$-Fe$_2$O$_3$ nanocubes were used as
sacrificial templates [108]. The average size of the carbon nanoboxes was approximately 80 nm and the thickness of the MoS2 shell was around 35 nm. The C@MoS2 nanoboxes exhibited a high specific capacity of about 1000 mA h g\(^{-1}\), remarkable cycling stability (952 mA h g\(^{-1}\) over 200 cycles at 0.4 A g\(^{-1}\)) and superior rate capability (531 and 403 mA h g\(^{-1}\) at 4 and 8 A g\(^{-1}\), respectively) as the anode in LIBs [108]. The high performance of this hybrid nanostructure was attributed to the relatively high electrical conductivity provided by the N-doped carbon nanoboxes and the buffering of volume changes during electrochemical reactions by the hollow carbon structure.

Besides the C@MoS2 nanoboxes, carbon nanofibers (CNFs) have also been reported to be decorated with MoS2 nanosheets (CNFs@MoS2) through a facile hydrothermal route using uniform carbonaceous nanofibers as supports (Fig. 3d) [109]. The CNFs@MoS2 nanocomposites showed a cable-like morphology with three to five layers of curly MoS2 nanosheets on the surfaces of CNFs. The surface area reached as high as 176 m\(^2\) g\(^{-1}\), owing to the hierarchically porous structure in the hybrid nanomaterials. In this design, the CNFs offered efficient electron pathways for rapid lithiation/delithiation processes. Meanwhile, the MoS2 sheath helped to increase the active surface area and promote rapid charge-transfer reactions. Moreover, this hybrid nanostructure could trigger new electrochemical Li\(^+\)-storage processes with a persistent transformation from Mo (or MoS\(_2\)) to MoS\(_4\), leading to a continuously increasing capacity during cycling. As an anode material for LIBs, the CNFs@MoS2 composite manifested a high capacity of 1264 mA h g\(^{-1}\) after 50 cycles at a current density of 0.1 A g\(^{-1}\) and still retained a capacity of 860 mA h g\(^{-1}\) at the high current density of 5 A g\(^{-1}\) [109].

Figure 3e presents a 2D nanosheets-on-carbon nanosheet hybrid structure, in which 2D mesoporous carbon nanosheets that could be further converted into mesoporous graphene nanosheets by a carbonization process were hybridized with TMO or TMD nanosheets [110,111]. This type of hybrid nanomaterial possesses high surface area, large interfacial contact area, efficient ion transport and inhibited volume expansion. Jiang et al. reported the fabrication of 2D Mo\(_2\)S\(_4\)-mesoporous carbon (Mo\(_2\)S\(_4\)/m-C) with a hybrid nanoarchitecture and an ideal atomic-level interface, in which the single-layer Mo\(_2\)S\(_4\) nanosheets and the m-C were sandwiched in an alternating sequence into a Mo\(_2\)S\(_4\)/m-C superstructure [111]. As shown in Fig. 3e, few-layer Mo\(_2\)S\(_4\) nanosheets were first synthesized by a hydrothermal reaction between Na\(_2\)MoO\(_4\) and thiourea in the presence of oleic acid (OA). Mo\(_2\)S\(_4\)/m-C hybrid nanosheets were then obtained by annealing Mo\(_2\)S\(_4\)/polydopamine (Mo\(_2\)S\(_4\)/PDA) precursor formed by a self-polymerization of dopamine with OA on the surface of Mo\(_2\)S\(_4\) nanosheets. The obtained hybrid nanosheets had a thickness of around 7.5 nm and an interlayer spacing of ~0.98 nm between adjacent Mo\(_2\)S\(_4\) nanosheets. Moreover, the specific surface area was measured to be 128 m\(^2\) g\(^{-1}\) with a pore volume of 0.27 cm\(^3\) g\(^{-1}\)—much higher than for the annealed Mo\(_2\)S\(_4\) nanosheets (17 m\(^2\) g\(^{-1}\)) and the Mo\(_2\)S\(_4\)/graphene nanocomposite (71 m\(^2\) g\(^{-1}\)). This hybrid nanostructure can address many issues for Mo\(_2\)S\(_4\)-based anode electrodes, such as low conductivity, unexpected self-aggregation, significant volume expansion and the accompanying polysulfide shuttle effect. Electrochemical tests demonstrated that the Mo\(_2\)S\(_4\)/m-C superstructure nanosheets exhibited a maximum reversible specific capacity of 1183 mA h g\(^{-1}\) at a current density of 200 mA g\(^{-1}\)—a superior rate capability (943 mA h g\(^{-1}\) at 6400 mA g\(^{-1}\)) and a stable cycling life (1023 mA h g\(^{-1}\) after 500 cycles at 400 mA g\(^{-1}\)). Beyond that, they also found that the capacity increased with increasing operating temperature of the LIBs, which reached 900 and 1280 mA h g\(^{-1}\) at a rate of 400 mA g\(^{-1}\) at a low temperature (3°C) and a high temperature (50°C), respectively [111].

Overall, 2D nanosheets hybridized with nanocarbon materials exhibited significantly improved lithium-storage capacities for LIB application. The deposition or incorporation of 2D metal oxide or sulfide nanosheets on various carbon nanomaterials can give these electrodes similar advantages to those of graphene, such as preventing self-restacking, accommodating volume changes, improving electrical conductivity, etc. This strategy is easily achievable because a wide range of carbon sources (e.g. glucose, glycol and carbon-containing polymers) can be directly used to coat the TMD/TMO nanosheets, and numerous nanostructures with specific shapes (e.g. fiber-like, sheet-like and other shapes) can be loaded onto the 2D nanosheets to form various heterostructures. Hence, in contrast to the sheet-like graphene, hybridization of 2D nanomaterials with carbon nanomaterials is more appealing, as they can form complicated shape-defined nanoarchitectures and sometimes their overall cost is relatively lower.

**2D nanomaterials hybridized with carbon nanotubes**

Carbon nanotubes (CNTs) are typical 1D carbon nanostructures and feature excellent electric conductivity, outstanding mechanical properties and
superior chemical stability. Depending on the wall structure, CNTs can be classified as single-walled nanotubes (SWNTs), in which a single graphite sheet is rolled into a cylindrical nanotube along the sheet plane directions, and multi-walled nanotubes (MWNTs) [112]. In contrast to the semiconducting graphite, CNTs are either metals or semiconductors and the electrical conductivity of MWNTs is reported to be around $2.5 \times 10^2$ to $2.0 \times 10^5$ S cm$^{-1}$ [113,114], which allows them to act as a conductive medium and fast transmission channel network for TMO or TMD nanosheets.

The synergism of these nanosheets with the robust and conductive CNTs is very helpful for maintaining the integrity of electrodes besides providing enhanced electric conductivity. Huang et al. proposed a facile, flexible and large-scale technique to synthesize leaf-like mesoporous CuO nanosheets-CNT 3D-network (CuO-CNT) nanocomposites (Fig. 4a) via the electrostatic interactions between the pre-oxidized CNT (negatively charged) and the colloidal CuO nanosheet solution (positively charged) [115]. As an anode material for high-performance LIBs, the CuO-CNT nanocomposite...
in a ratio of 8:2 delivered excellent capacity after 40 cycles, 571 mA h g⁻¹, which was ~2.3 times that of pristine mesoporous CuO nanosheets after 40 cycles (244 mA h g⁻¹) at a current density of 67 mA g⁻¹. It was also demonstrated that the introduction of CNTs was conducive to the enhancement of rate capability and reversibility with the increasing electrical conductivity [115].

The growth of ultrathin nanosheets on the surfaces of CNTs to form hierarchical hybrid structures is another approach to reaching outstanding capacity and rate capability. The CNT core-network can improve the overall electrical conductivity and stabilize the nanosheets after growth, while the hierarchical structure possesses a high surface area with enough space to alleviate the strain generated by repeated charging/discharging processes. Yu et al. reported a hierarchical nanostructure (CNTs@V₂O₅) with highly interconnected V₂O₅ nanosheets (NSs) deposited on CNT skeletons by a hydrothermal synthesis method. [116]. The V₂O₅ nanosheets had a thickness of around 10–20 nm and diameters of 50–100 nm (Fig. 4b). This CNTs@V₂O₅ hierarchical cathode material for LIBs exhibited an outstanding long cycling life, with 137-116 mA h g⁻¹ retained after 400 cycles at high rates (20C to 30C) in a voltage window between 2.0 and 4.0 V.

Similarly, hierarchical NiO and TiO₂-B nanosheets coated on the surfaces of CNTs were developed for lithium storage by Xu et al. [117] and Chen et al. [118], respectively. The ultrathin NiO nanosheets on bamboo-like amorphous CNTs (NiO@CNT) were fabricated by the calcination of α-Ni(OH)₂ nanosheets grown in situ on sulfonated polymeric nanotubes (PNTs) at 500°C for 4 h (Fig. 4c). This hybrid material delivered a large discharge capacity of up to 1034 mA h g⁻¹ after 300 cycles at a relatively high rate of 800 mA g⁻¹ [117]. Composites of TiO₂-B nanosheet arrays on carbon nanotubes (CNTs@TiO₂-B NSs) were prepared through a fast microwave-assisted solvothermal (MAS) route by using an imidazolium-based ionic liquid ([Bmim][BF₄]), which served as a guiding agent to interact with CNTs via cation-π interactions and further guide the in-situ growth of TiO₂-B nanosheet arrays on the CNT surfaces (Fig. 4d). From a Brunauer-Emmett-Teller (BET) calculation, this hybrid showed a specific surface area as high as 151.2 m² g⁻¹. When fabricated as the working electrode for batteries (Fig. 4e), the CNTs@TiO₂-B composite maintained a reversible capacity of 147 mA h g⁻¹ at the high current density of 6 A g⁻¹, which corresponds to ~36 C for anatase [118].

In addition, a MoS₂-SWNT hybrid thin film electrode was developed by Wang et al. via a facile filtration/wet transfer technique, where liquid-phase exfoliated MoS₂ nanosheets were deposited onto nitrocellulose membranes through vacuum filtration and then the thin film was transferred onto a Cu foil to form the electrode for LIBs, as shown in Fig. 4f [119]. Electrochemical tests showed that the capacity of the MoS₂-SWNT composite film with a thickness of 1 μm was about 992 mA h g⁻¹ over 100 cycles, although the capacity of the film with a thickness of 4 μm was only 600 mA h g⁻¹ after 100 cycles at the same rate, because the ion diffusion length and migration lengths are longer in thicker films.

In short, the 3D networks based on 1D tube-like CNT and 2D metal oxide or sulfide nanosheets have shown promising effects towards enhancing lithium-storage properties, especially the cycling and rate performances of electrodes. First, the 3D CNTs play a crucial role in the nucleation, growth and formation of centers of fine metal oxide/sulfide micro/nanostructures with uniformly distributed and defined morphologies on their surfaces. Second, 3D CNT networks act as interconnected electrically conductive skeletons, offering the benefits of shorter charge carrier diffusion lengths and increased electrical conductivity of the electrode. Third, these networks help to maintain the porous structure, facilitating fast mass transport for ions through the electrolyte in the middle. Finally, the excellent mechanical properties of CNTs can suppress the volume changes that occur during repeated charging/discharging cycles. Some major challenges still remain for the 2D-CNT hybrid nanomaterials. For example, the walls of CNTs are chemically inert and highly hydrophobic, which prevents the uniform growth of nanosheets on the pristine CNTs and results in a weak interaction between the TMO/TMD nanosheets and the CNTs.

### 2D nanomaterials hybridized with organic conductive polymers

Some polymers, including polypyrrole (PPy), polycrylonitrile (PA), polythiophene (PTH) and polyaniline (PANI), are rendered conductive by the conjugated bond systems along their backbones [120]. The main reason why these polymers are attractive for 2D hybrid electrode materials is their high charge density. For example, similar to the sandwich-like graphene-based nanostructures, ultrathin polypyrrole/SnS/polypyrrole (PPy/SnS/PPy) hybrid nanosheets were synthesized via a facile hydrothermal reduction and in-situ polymerization route by using uniform ZnSn(OH)₆ microcubes as the tin source, as reported by Liu et al. (Fig. 5a) [121]. The ultrathin 2D structure of the
Figure 5. 2D nanomaterials hybridized with conductive polymers or metallic nanoparticles. (a) Schematic drawing of the synthesis of sandwich-like SnS/PPy ultrathin nanosheets from ZnSn(OH)\(_6\) microcubes [121] (Copyright 2016, American Chemical Society); (b) rate capability of SnS-based anodes for LIBs [121] (Copyright 2016, American Chemical Society); (c) cycling performance of the sandwich-stacked SnO\(_2\)/Cu nanosheets [130] (Copyright 2013, American Chemical Society); (d) schematic drawing of the roll-up and compression approach for the sandwich-structured SnO\(_2\)/Cu hybrid nanosheets [130] (Copyright 2013, American Chemical Society); (e) schematic configuration of a multichannel battery with sandwich-structured SnO\(_2\)/Cu/CB nanosheets [130] (Copyright 2013, American Chemical Society).

electrochemically active SnS facilitated Li\(^+\) diffusion, while the highly conductive PPy layer on both sides of the SnS nanosheets ensured fast electron transport. As the anode material for LIBs, an extremely high reversible capacity of approximately 1000 mA h g\(^{-1}\), which was very close to the theoretical capacity of around 1138 mA h g\(^{-1}\), could be achieved at a current density of 100 mA g\(^{-1}\) within a voltage range of 0.01-3.0 V (Fig. 5b). Furthermore, the capacity retention was outstanding, with a high
capacity of 703 mA h g⁻¹ at 1 A g⁻¹ after 500 cycles [121].

Similar designs combining the merits of graphene/graphene oxide, metal oxides or chalcogenides with conductive polymers have been reported as electrodes for other energy-storage devices (e.g. supercapacitors), such as sandwich-structured MnO₂/polyaniline/reduced-graphene oxide (MnO₂/PPy/rGO) hybrid composites [122], 2D GO-based mesoporous PPy nanosheets (mPPy@GO) [123], rGO/MnO₂/PPy ternary film electrode [124], sandwich-like polyaniline/graphene (PANI/G) [125], etc. In those 2D hybrid nanomaterials obtained by hybridizing with conductive polymer, the electrochemical performance has been significantly enhanced.

Generally, the hybridization of 2D nanomaterials with conductive polymers to form organic-inorganic hybrids is capable of attaining higher capacities and shorter charging times compared with other conductive substrates due to their remarkable synergistic effects. This strategy, however, is still far from practical application, predominantly due to their unsatisfactory structural stability. On the one hand, the electrical conductivity of these conductive polymers is difficult to control during polymerization reactions, owing to the possible thermal degradation at elevated temperatures, the contraction of the conducting islands caused by cross-link reactions, the evaporation or segregation of the dopants or the existence of the non-conductive residual precursors [126]. On the other hand, the polymer structures are easily destroyed over repeated cycles, leading to slow transfer of ions and low capacity retention. Additionally, the mechanical performance of conductive organic polymers is inferior to those of graphene and CNTs, which has a negative effect on the electrode integrity in LIB application. Therefore, further work is still needed for the optimization of both the fabrication techniques for 2D nanosheets–organic conductive polymer hybrid nanomaterials and the proper structural designs for energy-storage device electrodes.

### 2D nanomaterials hybridized with metallic nanomaterials

Some metallic nanomaterials, including Ag [127–129], Cu [130], Au [131], Ni [132,133], etc., are also employed as a conductive matrix to form 2D TMO/TMD/semiconductor–metal nanocomposites. Among them, Ag nanoparticles (NPs) are the most widely studied ones due to their excellent intrinsic electrical conductivity. Ag NPs also offer higher rigidity and lower deformability compared to carbon, which is beneficial to effectively preserve the morphology of the as-obtained hybrid nanoarchitecture. Furthermore, the presence of Ag NPs on the surfaces of 2D nanosheets provides increased interlayer spacing for easy lithium-ion intercalation.

Pan et al. reported a coordination-driven ex-situ hierarchical assembly of Ag NPs on MoS₂ nanosheets with the help of mercaptosuccinic acid (MSA) [127]. This multifunctional organic acid can bond to Ag NPs through an Ag–S covalent linkage and a carboxylate group, and it can link to the sulfur atoms of the MoS₂ nanosheets through mutual coordination to Cu²⁺ ions. Via this coordination-driven linkage, the interaction between Ag NPs and MoS₂ nanosheets is much stronger than the conventional weak bonds, such as via van der Waals forces. Even when the mass fraction of Ag nanoparticles was only 5%, the Ag–MoS₂ hybrid nanosheets delivered a high reversible capacity of 920 mAh g⁻¹ at the rate of 100 mA g⁻¹ [127].

Later, the co-assembly of Ag and Fe₃O₄ NPs on MoS₂ nanosheets for anode and the self-organization of Ag NPs and TiO₂ nanorods on V₂O₅ nanosheets for cathode were also explored to enhance lithium storage [128]. Besides the ex-situ Ag NP decoration, Hao et al. developed a method for directly de-alloying well-designed CoAgAl alloys in alkaline solution to fabricate flower-like Co₃O₄/Ag nanosheets [129]. Owing to the unique structure and enhanced conductivity, the nanocomposite presented much improved cycling stability with increasing Ag content. After 1000 cycles, high capacity retention of 90.0% compared to the 31st cycle was found. Strikingly, the electrode could still retain stable reversible capacities of ~460 and 390 mA h g⁻¹, even at high rates of 2.0 and 3.0 A g⁻¹, respectively [129].

Rolling up nanosheets with a subsequent compression process was also introduced to prepare compact sandwich-like SnO₂/Cu nanosheet stacks [130]. As shown in Fig. 5d, the composite was obtained by compressing the rolled-up SnO₂/Cu bilayer films with pre-coated carbon black (CB), which acted as an intersheet spacer to protect the composite from self-agglomeration and to ease volume expansion during repeated charge/discharge cycles. When tested as electrode material for LIBs, the multichannel anodes based on 2D SnO₂/Cu hybrid nanosheets exhibited a high reversible capacity of 764 mA h g⁻¹ at a current density of 0.1 A g⁻¹ and maintained 572 mA h g⁻¹ at a rate of 0.1 A g⁻¹ after 100 cycles (Fig. 5c and e) [130].

In summary, these metallic nanoparticles hybridized with 2D nanomaterials could enhance the electrochemical performance when used as electrode materials for lithium storage, by taking advantage of the native merits of the metallic...
nanoparticles, including good electrical conductivity and excellent structural stability. It is obvious, however, that the cost might be one of the main barriers for the practical application of this type of hybrid nanomaterial. Moreover, further research is needed to achieve the homogeneous dispersion of metal NPs on the surfaces of TMD/TMO nanosheets.

**STRATEGY 2: EDGE/SURFACE FUNCTIONALIZATION**

As is well known, some challenges still remain for the direct utilization of 2D nanosheets in energy-storage devices. Pristine graphene, with higher activity at the edges than on the surfaces, has an inferior chemical affinity to other nanomaterials, resulting in poor interfacial compatibility, long diffusion paths and slow chemical reactivity. For lithium-ion storage, it also suffers from large irreversible capacity, low initial Coulombic efficiency and fast capacity fading, as well as large hysteresis between charge-discharge curves as a result of its intrinsic skeleton structure and strong tendency towards restacking during the battery assembly. In terms of layered TMD/TMO nanosheets, the repeated insertion/extraction of Li\(^+\) ions often gives rise to dramatic variations in the interlayer spacing, along with successive phase transitions. To address these issues, edge/surface functionalization of 2D nanomaterials has proved to be effective for modifying many physical properties, including the intrinsic conductivity and band structure [134]. For high-performance LIB applications, this strategy is mainly achieved by the introduction or elimination of certain atoms, ions or bonds to improve their electronic properties, interface structures or chemical activities to accommodate the repeated intercalation/de-intercalation of lithium ions during charging/discharging processes.

**Edge/surface functionalization via doping**

This strategy mainly involves the doping of active atoms or ions into graphene and TMO nanosheets to improve their electrochemical properties as electrode materials for LIBs. The most common and typical category is heteroatom-doped graphene. To overcome the structural limitations of the graphene skeleton, some heteroatoms, such as N, F, Cl, Br, S, P, B, etc., are introduced into the graphene framework with expectations of changing the surface adsorption energy, reducing the ion diffusion barrier and thus enhancing the battery performance. Furthermore, these doped graphene-based nanomaterials could deliver a higher theoretical capacity than the pristine graphene, owing to the synergic storage mechanism with heteroatoms. Liao et al. studied the effect of edge-doping of B, C, N and O onto zigzag graphene nanoribbons and found that the maximal loading of charges/carriers onto graphene obeys a rule of [8-\(n\)-1], where \(n\) is the number of valence electrons of the edge-site atom that constitutes the adsorption site [135,136]. If metal atoms (Cr, Mn, Fe, etc.) were used as the doping elements, the graphene could also be curved again to form metal-welded CNTs with enhanced electrochemical properties [137].

Fluorine (\(\chi = 3.98\)) is the most electronegative element in the periodic table—much higher than carbon (\(\chi = 2.55\)). Moreover, the C–F bond is the strongest single covalent bond (488 kJ mol\(^{-1}\)). As a result, fluorine-doped graphene nanomaterials could offer the highest charge polarization to enhance electrochemical activities and superior electrode stability.

To obtain high-quality fluorine-doped graphene, both liquid exfoliation (Fig. 6a) and dry-milling methods (Fig. 6c) were investigated in previous reports [138–140]. In contrast to the liquid exfoliation of graphite into graphene nanosheets, most fluorine-doped graphite could not be easily exfoliated in the common solvents, such as N-methyl-pyrrolidone (NMP) and N,N-dimethylformamide (DMF), under the same conditions. Zhan et al. obtained fluorine-doped graphene via an ultrasonic treatment of fluorine-doped graphite in 2-isopropanol (IPA) solvent at room temperature [138]. The product was shown to have a high fluorine content of 49.7 at% and a specific surface area of 125 m\(^2\) g\(^{-1}\), as well as a thickness of approximately 10 nm. In LIBs, as demonstrated in Fig. 6b, these nanosheets exhibited a reversible capacity of 780 mA h g\(^{-1}\) after 50 cycles at a current density of 50 mA g\(^{-1}\). Most importantly, the reversible capacity of fluorine-doped graphene was 626 and 336 mA h g\(^{-1}\) at the high current densities of 0.1 and 0.5 A g\(^{-1}\), respectively—much higher than for fluorine-doped graphite (218 and 108 mA h g\(^{-1}\)) [138].

Another example of liquid exfoliation of fluorine-doped graphite was achieved in acetonitrile (ACN) and chloroform solvents through a solvothermal exfoliation approach by Sun et al. [139]. The two chosen organic solvents have low boiling points and presented no reduction effect on the C–F bonds at high pressure and temperature. When these nanosheets were utilized as electrode materials for the LIBs, high-rate capability and high discharge voltage were realized with a maximum specific capacity of 775 mA h g\(^{-1}\) at a rate of 0.05 C, along with a power density of 4038 W kg\(^{-1}\) at 3 C [139]. For this technique, the
selection of proper solvents for effective exfoliation is crucial; however, suitable solvents are extremely limited, which has greatly hindered progress towards large-scale production. On the contrary, the simple and low-cost dry ball-milling technique can avoid the use of harmful organic solvents and has great potential to be scaled up (Fig. 6c).

Besides edge-fluorinated graphene by diluted fluorine gas in argon, other heteroatom-edge-doped graphene nanoplatelets (XGnPs, X = Cl, Br, I, N, S, H, etc.) have also been successfully synthesized via dry-milling graphite in the presence of the dopant element, including chlorine (Cl$_2$), bromine (Br$_2$), iodine (I$_2$), nitrogen (N$_2$), sulfur (S), hydrogen (H$_2$), etc. [140–144]. When studied for their reversible Li-ion intercalation properties, Jeon et al. found that FGnPs delivered a specific capacity of 650.3 mA h g$^{-1}$—higher than that of the reference edge-hydrogenated GnPs (HGNPs), with a capacity of 511.3 mA h g$^{-1}$ at 0.5 C within the voltage range of 0.02–3 V. Furthermore, 76.6% capacity retention could be achieved after 500 cycles, indicating excellent cycling performance [144]. Xu et al. compared the discharge capacities of HGNPs, ClGNPs, BrGNPs and IGNPs in the voltage range of 0.02-3.0 V, which were 1666.9, 1783.6, 1690.4 and 1750.3 mAh g$^{-1}$, respectively, as shown in Fig. 6d. Furthermore, IGNP showed a higher rate capacity than the others at specific current $\geq$ 0.5 C (inset of Fig. 6d), which was attributable to the higher electronegativity of I ($\chi = 2.66$) than carbon, its high surface area (736.8 m$^2$ g$^{-1}$) and the improved Li$^+$ insertion/extraction at the edges between the graphitic layers [142].

Beyond the widely studied fluorine atom doping, nitrogen atoms were also embedded into the graphene framework to form NG nanosheets. The implantation of nitrogen atoms significantly changes the electronic properties of graphene, provides more active sites, improves the interactions between...
carbon and lithium ions, and thus enhances the lithium diffusion and transfer kinetics during LIB application. Reddy et al. reported the controlled growth of NG layers on copper current collectors by a liquid-precursor-based chemical vapor deposition (CVD) technique [145]. As electrode materials for LIBs, these NG films delivered a reversible discharge capacity of 0.05 mA h cm$^{-2}$ — higher than that of pristine graphene (0.03 mA h cm$^{-2}$) — at a current density of 5 μA cm$^{-2}$ within a voltage window between 3.2 and 0.02 V. Even at the very high current rate of 100 μA cm$^{-2}$, 60% of the capacity could be retained [145]. Wang et al. synthesized NG nanosheets by thermal treatment of graphite oxide under ammonia at 800°C for 2 h [146]. The nitrogen-doping level of these nanosheets was around 2%, constituting 57.4% pyridinic, 35.0% pyrrolic and 7.6% graphitic nitrogen atoms. Galvanostatic charge/discharge tests revealed that these N-doped graphene-based electrodes exhibited a high reversible capacity of about 900 and 250 mA h g$^{-1}$ at a current density of 42 and 2100 mA g$^{-1}$, respectively [146]. Huang et al. prepared nitrogen and fluoride co-doped graphene (NFG) with 3.24 at % nitrogen and 10.9 at % fluorine contents via a one-step hydrothermal reaction between graphene oxide (GO) and trimethylamine tri(hydrofluoride) [(C$_2$H$_5$)$_3$N·3HF], where (C$_2$H$_5$)$_3$N·3HF served as the nitrogen and fluorine source [147]. When tested as anode material for lithium-ion storage, NFG showed remarkable reversible discharge capacities and rate capability, with capacities of 1075 and 305 mA h g$^{-1}$ at current densities of 0.1 and 5.0 A g$^{-1}$, respectively, as well as high capacity retention of around 95% at the rate of 5.0 A g$^{-1}$ over 2000 cycles [147].

Besides heteroatom-doped graphene, ion-doped TMO nanosheets were also explored as electrode materials for high-performance LIBs. It has been reported that the doping or intercalation of some cations (e.g. K$^+$, Na$^+$, Sn$^{2+}$, V$^{4+}$, etc.) into the layered TMOs could help increase the electronic conductivity of the resultant ion-doped nanomaterials, enhance the diffusion of lithium ions and thereby improve the electrochemical storage performance [148]. Moreover, the incorporation of various cations into the layered nanosheets is helpful for increasing the interlayer spacing to make ion insertion more efficient. Lu et al. reported 3D M$_x$MnO$_2$ (M = Li, Na, K, Co and Mg) cathodes with a variety of metal ions intercalated into the layered MnO$_2$ nanosheets (Fig. 6e) [149]. Electrochemical tests demonstrated that the specific capacities of LiM0, NaM0, KMO, MgMO and CoMO were about 118, 137, 155, 97 and 87 mA h g$^{-1}$, respectively, for lithium storage at a current density of 30 mA g$^{-1}$.

In rate capability testing, as shown in Fig. 6f (left), KMO possessed the best reversible capacity retention of around 61%, compared with LiMO (50%), NaMO (58%), MgMO (48%) and CoMO (45%). Nevertheless, as presented in Fig. 6f (right), the NaMO electrode maintained the highest stability, with about 74% of the initial capacity at 80 mA g$^{-1}$ after 500 cycles. These different electrochemical behaviors are related to the types of doped cations. Compared with divalent cations (e.g. Co$^{2+}$), monovalent cations, including K$^+$, Na$^+$ and Li$^+$, were more favorable for enhancing the lithium-ion storage performance [149].

**Surface functionalization via defects**

The presence of abundant defects (e.g. point defects, grain boundaries or in-plane heterojunctions, etc.) could result in vacancies or stress on the basal planes of 2D nanosheets and thus dramatically increase the exposure rates of active sites, hence greatly increasing their ability to accommodate the insertion and diffusion of Li$^+$ ions. Moreover, defects have the benefit of enhancing the electrical conductivity of 2D nanomaterials, particularly for most TMD and TMO nanosheets. These defects are mainly introduced into the 2D nanomaterials by two types of synthetic approaches, namely direct growth using chemical vapor transport (CVT) and CVD, together with some post-treatments, such as plasma treatments, ion/electron irradiation and high-temperature annealing under different gases [150].

Hydrogenated TMOs with oxygen vacancies as an important representative of defect-functionalyzed 2D nanomaterials have been paid much attention by virtue of their enhanced electrical conductivity, structural stability and electrochemical reaction kinetics towards the diffusion of lithium ions [151–154]. For example, in V$_2$O$_5$, four types of oxygen sites are bonded with one vanadium atom in an isolated layer. In lithium-ion storage applications, there are three potential paths for Li$^+$ diffusion, as indicated in Fig. 7a. Among them, Path A is considered to be the easiest route and the diffusion of Li$^+$ will become more efficient with the creation of oxygen defects at O(II) sites along Path A. The experimental realization of O(II) defects, however, is difficult to achieve due to the higher binding energy for O(II) atoms. Peng et al. synthesized hydrogenated V$_2$O$_5$ (H-V$_2$O$_5$) nanosheets with most oxygen vacancies at O(II) sites by treating V$_2$O$_5$ nanosheets in H$_2$ atmosphere at 200°C [154]. Under the H$_2$ environment, hydrogen was initially adsorbed at the oxygen sites to form OH groups and then the O(II) vacancies were formed by the removal of OH groups.
When evaluated for LIBs, the as-obtained H-V2O5 nanosheets exhibited a discharge capacity as high as 259 mA h g⁻¹ over the first cycle at a current density of 100 mA g⁻¹ and retained 55% of their capacity when the rate was increased by 20 times to 2.0 A g⁻¹ in the potential range of 2.0–4.0 V. Only 0.05% capacity decay per cycle was observed after the first 30 cycles. This superior lithium-storage performance was attributed to the effective activity of oxygen defects at the bridging O(II) sites towards lithium-ion diffusion and storage [154].

Defect-rich TMDs, especially MoS₂ nanosheets, were also reported as high-performance electrode materials. The native defects of MoS₂ nanosheets, including the common sulfur vacancies (Vₛ), sulfur interstitials (Sᵢ), molybdenum vacancies (Vₘₒ), and molybdenum interstitials (Mₒ), can modulate the electronic properties by altering the charge carrier mobility and density [155–157]. Defect-rich MoS₂ ultrathin nanosheets with ample unsaturated sulfur atoms were fabricated by using a stoichiometric ratio of Mo(VI) to L-cysteine and 1,6-hexanediamine was chosen as the coordinating agent [158]. These nanosheets had a thickness of 8–9 nm, corresponding to 13–15 sandwiched S–Mo–S layers. When applied as the anode for LIBs, the reversible discharge capacity could be maintained at 589 mA h g⁻¹ after 80 cycles at a current density of 100 mA g⁻¹ [158].

Zhang et al. demonstrated a facile and scalable route to synthesize a flexible, free-standing, defect-rich MoS₂/graphene/CNT (dr-MGC) hybrid paper, in which ultrathin defect-rich MoS₂ nanosheets (dr-MoS₂ NSs) were uniformly incorporated into conductive graphene/CNT frameworks via vacuum filtration and thermal reduction process [159]. These nanosheets showed a typical lamellar structure with a thickness of about 3–5 nm and a lateral size between 100 and 200 nm. Owing to the synergistic effects of defects and hybridization, the flexible hybrid paper presented a high reversible capacity of 1137.2 mA h g⁻¹ at a current density of 0.1 A g⁻¹ with a voltage window from 0.01 to 3.0 V.

Chen et al. reported the successful design of 2D sandwich-like carbon-coated ultrathin TiO₂@defect-rich MoS₂ hybrid (UT-TiO₂/C@DR-MoS₂) nanosheets [160] via a glucose-assisted hydrothermal reaction at 200 °C [160]. As illustrated in Fig. 7b, glucose molecules nucleated on the rough surfaces of UT-TiO₂ and the absorbed MoO₄²⁻ was reduced in situ to MoS₂ in the presence of thiourea (C₄N₂H₄S). After the reaction time was prolonged to 24 h, the glucose molecules were carbonized completely to form defect-rich MoS₂ nanosheets. When these nanosheets were assembled as anodes for LIBs, they delivered an excellent rate capability (785.9, 585.6, 507.6 and 792.3 mA h g⁻¹ at 0.1, 1.0, 2.0 and 0.1 A g⁻¹, respectively) and superior cycling performance (805.3 mA h g⁻¹ at 0.1 A g⁻¹ after 100 cycles). Figure 7c presents a molecular structure model for the Li-insertion process to demonstrate the lithium-storage mechanism. In the first discharge step, the defect-rich MoS₂ with ample additional edge sites could shorten the diffusion paths and offer sufficient diffusion channels. After the first discharge, however, the MoS₂ nanosheets would break down into small nanoparticles and were further transformed into smaller amorphous Mo and S nanoclusters that
were deposited on the TiO$_2$@C structure. This breakdown is helpful for increasing the contact area between the electrolyte and electrode materials, and providing more channels for Li$^{+}$ diffusion, thus further enhancing the lithiation kinetics [160].

To summarize, the main purpose for the strategy of edge/surface functionalization is to overcome the intrinsic structural limitations of graphene, metal oxide or metal sulfide nanosheets to make the diffusion and transfer of ions and charges more efficient. Via doping with atoms or ions, as well as the formation of defects, the electrical properties can be tuned to facilitate much more rapid intercalation/de-intercalation behavior. The accurate control of doping levels (e.g. atomic-level concentrations) and the formation of specific types of defects at desired locations, however, are still very challenging. Moreover, how to obtain massive amounts of uniform products with stable doping levels and homogenous distribution of defects needs a deeper understanding and further exploration.

**STRATEGY 3: STRUCTURE OPTIMIZATION**

Structure optimization is an essential strategy for improving the lithium-storage properties for LIBs, including thickness regulation, porosity manipulation and morphology modulation. In the case of 2D layered nanosheets, their electrochemical properties have found to be dependent on the overall thickness and thus thickness regulation is one tangible approach to enhance lithium-storage performance. The introduction of porous structures also makes these nanosheets more appealing, with more exposed active sites and better ability to buffer volume expansion during electrochemical reactions. Moreover, 3D hierarchical structures assembled from 2D ultrathin nanosheets or the related heterostructures can offer high surface area for effective electrochemical reactions and various types of pores for high-efficiency lithium-ions diffusion. By modulating the morphology and structure of 2D nanomaterials, the reversible capacity at high rates and the cycling stability during charging/discharging processes in LIBs are expected to be significantly enhanced.

**Structure optimization via thickness regulation**

In the case of 2D nanomaterials, thickness is highly correlated with their many physical or chemical properties, such as band structure, wettability, out-of-plane transport, etc., which will strongly influence the lithium-storage performance in energy device applications, even though there has been no direct research on this aspect at present [161–170].

One typical example is that the band structure of graphene, which is directly associated with its electrical properties, is changed from the metallic state to the semiconductive state as the number of stacking layers increases. Another example is that monolayer MoS$_2$ nanosheets possess very strong photoluminescence, which is absent in their corresponding bulk forms, indicating the thickness-dependent electronic structures of the 2D nanomaterials [168,169]. These results indicate that the thickness of 2D nanomaterials can result in different electrical properties in rechargeable batteries.

Wettability is another important property that must be considered in energy devices, because the wetting behavior between the electrode materials and electrolyte significantly affects the contact between the active materials and electrolyte, the ion diffusion and the formation of solid electrolyte interphase (SEI) films. Rafiee et al. demonstrated that graphene monolayer is wetting-transparent to various substrates, including copper, gold and silicon, but not glass. As the number of graphene layers increased, the contact angle of water on copper gradually increased (86.2° for monolayer) and finally saturated at the bulk graphite value (around 90.6°), which was reached for more than six graphene layers [170]. It therefore must be an interesting fundamental question as to how the stacking number or the thickness of the 2D nanomaterials influences the energy-storage performance of the materials. It is expected that thickness modulation will be an effective strategy to further improve the performance of energy-storage devices.

**Structure optimization via porosity manipulation**

The strategy of porosity manipulation is usually achieved by the introduction of porous structures into 2D nanosheets. It was demonstrated that porous ultrathin nanosheets represent a highly promising structure as electrode materials for LIBs. This is because the pores in the nanosheets can offer ample active sites and facilitate rapid diffusion of lithium ions. Furthermore, the sufficient open spaces within this structure are beneficial to suppress the volume changes during intercalation/disintercalation cycles [171–173].

Porous graphene (or called graphene nanomesh) has been prepared by a CVD method by using porous MgO sheets as template [174,175]. Nitrogen adsorption/desorption isotherms confirmed that the specific surface area of the porous
graphene can be as high as 1654 m² g⁻¹. The porous graphene with a pore size of 3–8 nm can effectively overcome the diffusion resistance and distance issues between graphene and lithium ions, and can provide more edges for enhanced Li⁺ storage. As a result, the porous graphene presented a high reversible capacity (1723 mA h g⁻¹ at 0.1 C) and an excellent high-rate capability (203 mA h g⁻¹ at 20 C) [175].

Wang et al. fabricated mesoporous NiO nanosheet networks (NSNs) with a thickness of over 5 μm and a pore size of around 5 nm on Ni foam by a combination of solvothermal reaction with subsequent calcination [176]. The mesopores embedded in the nanosheets play the role as buffering zones to accommodate the volume changes, while the macroporous networks promote the diffusion of electrolyte into the inner area of the electrodes, and thus enable rapid Li⁺ transport. As anodes for LIBs, these NSNs exhibited a reversible capacity as high as 1043 mA h g⁻¹ after 80 cycles at a current density of 0.2 C and a capacity of more than 305 mA h g⁻¹ at a rate of 10 C (1 C = 718 mA g⁻¹) in the voltage range between 0.02 and 3.0 V [176]. Later, 2D Co₃O₄ NSNs were fabricated using a similar technique by the same group (Fig. 8a and b) [177]. The thickness of these nanosheets was estimated to be about 10 nm and the height on the Ni foam was 5.8 μm. These networks could deliver a reversible capacity of 4.39 mA h cm⁻² (or 1058 mA h g⁻¹) after 30 cycles at a rate of 0.74 mA cm⁻² (or 178 mA g⁻¹) and as high as 1.61 mA h cm⁻² at a current density of 7.38 mA cm⁻² [177]. Mesoporous Co₃O₄ nanoplatelets were also synthesized for LIBs by thermal decomposition of Co(OH)₂ precursor [178,179]. When applied as anode materials, the nanoplatelets delivered a high specific capacity of 1203 mA h g⁻¹ initially and maintained 330 mA h g⁻¹ over 200 cycles at a current rate as high as 10 C [179].

Qin et al. prepared mesostructured N-doped MoS₂ nanosheets with a thickness of around 3 nm, a pore size ranging from 2 to 50 nm and a BET specific surface area of 110.5 m² g⁻¹ by a facile sol-gel approach with molybdenum chloride (MoCl₅) and thiourea ((NH₂)₂CS) as raw materials [180]. Electrochemical results indicated that the product revealed a high stable reversible capacity (998.0 mA h g⁻¹ at a current density of 50 mA g⁻¹ over 100 cycles) and a remarkable rate performance (610 mA h g⁻¹ at the high rate of 2 A g⁻¹). These results were superior to those for other MoS₂ nanomaterials with different morphologies, including nanoparticles (410 mA h g⁻¹ after 80 cycles), hollow particles (902 mA h g⁻¹ after 80 cycles) and nanoflakes (605 mA h g⁻¹ after 50 cycles) [180]. This higher capacity and cycling stability could be attributed to their large surface area, porous structure, increased interlayer distance and the effect of the nitrogen doping.

Structure optimization via morphology modulation

The construction of hierarchical structures/heterostructures is an effective method to avoid the self-restacking trend of 2D sheet-like nanomaterials and to make full use of the advantages of 2D nanomaterials [181]. The fabrication of hierarchical structures and heterostructures is often accompanied by the introduction of porous structures and extra reaction sites, which can further enhance the electrochemical performance [182].

Cao et al. fabricated 3D hierarchically porous α-Fe₂O₃ nanosheets by annealing the as-prepared FeOOH precursor on copper foil [183]. Besides the common advantages of the hierarchical structures, this in-situ-fabricated free-standing and aligned structure had a close contact between the nanosheets and the current collector, which facilitated rapid electron transport between the α-Fe₂O₃ nanosheets and the substrate. As a binder-free anode for LIBs, these nanosheets exhibited appealing electrochemical properties, delivering a reversible capacity of 877.7 mA h g⁻¹ at a current density of 2.01 A g⁻¹ over 1000 cycles and the capacity of 433 mA h g⁻¹ was still retained when the rate increased to 20.1 A g⁻¹ [183].

Hierarchical MoS₂ hollow nanospheres (HNS) were synthesized through the sulfurization of the precursor, highly uniform molybdenum-glycerate spheres (MoG), under solvothermal conditions [184]. The MoS₂ HNS possessed a uniform diameter of ~580 nm, a thickness of ~140 nm, a specific surface area of 31.5 m² g⁻¹ and a pore size distribution mostly below 10 nm. Furthermore, after annealing at 700°C in Ar/H₂ for 2 h, the hierarchical MoS₂ shells exhibited good structural stability without obvious distortion in appearance. Benefitting from their unique structural features, such as the ultrathin subunits and well-defined hollow interior to withstand the structural strain, the as-obtained HNS exhibited a high capacity of around 1100 mA h g⁻¹ at a current density of 0.5 A g⁻¹ without obvious capacity decay after 100 cycles and good rate retention (944, 895, 831, 762, 711 and 576 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, 2 and 5 A g⁻¹, respectively) (Fig. 8c) [184].

Liu et al. fabricated 3D hierarchical SnO₂ hollow spheres 220 nm in diameter that were assembled from 5-nm-thick SnO₂ nanosheets [185]. To further
improve their electrochemical properties, a thin carbon layer, with a thickness of 3 nm, was coated on the nanosheets to form SnO\textsubscript{2}/C composite. Combining the advantages of the low-dimensional nano-sized building blocks, the hollow structure and the elastic carbon buffering layer, the as-obtained composite delivered a discharge capacity of 900 mA\textperiodcentered h \textpermg \textsuperscript{-1} in the 50th cycle at a current density of 100 mA \textpermg \textsuperscript{-1}—much higher than those of bare SnO\textsubscript{2} (~607.2 mA\textpermg \textsuperscript{-1}) and commercial SnO\textsubscript{2} powders (382.0 mA\textpermg \textsuperscript{-1}) under the same conditions (Fig. 8d). Similarly, the SnO\textsubscript{2}/C maintained a stable discharge capacity of 670 mA\textpermg \textsuperscript{-1} at the high rate of 2.0 A \textpermg \textsuperscript{-1}, corresponding to an enhancement of 200 mA\textpermg \textsuperscript{-1} over the bare SnO\textsubscript{2} anode [185].

Chen et al. reported a rational design for hierarchical sandwich-type hybrid carbon nanosheets (SCNMM) composed of micro/mesoporous carbon and graphene layers through a double template by using GO and SiO\textsubscript{2} nanoparticles (NPs) as the shape-directing and pore-guiding agents [186]. In this typical synthetic routine, in-situ polymerization of poly(pyrrrole) on the surfaces of GO nanosheets was chosen as the method for forming a SiO\textsubscript{2}-NP-embedded carbon coating. Then, the porous structures were achieved by a carbonization step following by etching the SiO\textsubscript{2} NPs in HF and KOH solutions (Fig. 8e). These porous sandwiched carbon nanosheets possessed a thickness of around 10–25 nm, an ultrahigh surface area of 1588 m\textsuperscript{2} g\textsuperscript{-1} and a broad pore size distribution of 0.8–6.0 nm. Then, sulfur was impregnated into these nanosheets via the melt-diffusion method to generate S@SCNMM nanocomposite as cathode for lithium-sulfur batteries. The experimental results indicated that the as-prepared SCNMM with a mass ratio of 74% sulfur manifested a high second-cycle reversible capacity of 1370 mA\textpermg \textsuperscript{-1} at the rate of 0.5 C (1 C = 1675 mA\textpermg \textsuperscript{-1}), excellent cycling stability, with 860 mA\textpermg \textsuperscript{-1} retained at 1 C after 100 cycles, and good rate capability with 510 mA\textpermg \textsuperscript{-1} retained, even at a high rate of 10 C [186].

3D hierarchical heterostructures have also been extensively studied for energy-storage devices. It is very difficult to obtain highly uniform 3D hierarchical nanostructures, owing to the complicated nucleation and growth of the nanostructures on more than two different substances in the same system. Recently, Niu et al. developed a one-step gradient hydrothermal method to obtain a series of 3D hierarchical heterogeneous nanostructures with 2D constituents, including V\textsubscript{2}O\textsubscript{5}/NaV\textsubscript{6}O\textsubscript{15}, V\textsubscript{2}O\textsubscript{5}/ZnV\textsubscript{2}O\textsubscript{4}, and V\textsubscript{2}O\textsubscript{5}/CoV\textsubscript{2}O\textsubscript{4}, which was achieved via controlling the sequence of nucleation and growth of vanadium oxide and vanadium-based carbon nanosheet encasing sulfur (S@SCNMM) and mesoporous structure (SCNMM).
<table>
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<td>~560 mAh g⁻¹</td>
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<td>[99]</td>
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<tr>
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<td>NiO/G composites</td>
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<td>NiO size: 100–200 nm</td>
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<td>[107]</td>
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<td>403 mAh g⁻¹ (8.0 A g⁻¹)</td>
<td>952 mAh g⁻¹ after 200 cycles (0.4 A g⁻¹)</td>
<td>[108]</td>
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<td>&gt;94% (2nd)</td>
<td>&gt;670 mAh g⁻¹ (0.067 A g⁻¹)</td>
<td>&lt;100 mAh g⁻¹ (3.35 A g⁻¹)</td>
<td>571 mAh g⁻¹ after 40 cycles (0.067 A g⁻¹)</td>
<td>[115]</td>
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<td>CNT@V₂O₅ composites</td>
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<td>—</td>
<td>285 mAh g⁻¹ (1 C)</td>
<td>127 mAh g⁻¹</td>
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<td>[116]</td>
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<td>Solution-based route</td>
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<td>1377 mAh g⁻¹ (0.8 A g⁻¹)</td>
<td>775 mAh g⁻¹</td>
<td>1034 mAh g⁻¹ after 300 cycles (0.8 A g⁻¹)</td>
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<td>147 mAh g⁻¹</td>
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<td>[118]</td>
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<tr>
<td>MoS2-CNT films</td>
<td>Exfoliation &amp; mixing</td>
<td>—</td>
<td>—</td>
<td>1117 mAh g⁻¹ (0.1 Ag⁻¹)</td>
<td>670 mAh g⁻¹ (3.2 Ag⁻¹)</td>
<td>992 mAh g⁻¹ after 100 cycles (0.1 Ag⁻¹)</td>
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<tr>
<td>SnS/polyurrole nanosheets</td>
<td>In situ polymerization</td>
<td>Sandwich-like</td>
<td>g~59.4% (1st)</td>
<td>1828 mAh g⁻¹ (0.1 Ag⁻¹)</td>
<td>576 mAh g⁻¹ (5.0 Ag⁻¹)</td>
<td>703 mAh g⁻¹ after 500 cycles (1.0 Ag⁻¹)</td>
<td>[121]</td>
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<td>Ag–MoS2 hybrid</td>
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<td>—</td>
<td>&gt;1600 mAh g⁻¹ (0.1 Ag⁻¹)</td>
<td>&gt;500 mAh g⁻¹ (5.0 Ag⁻¹)</td>
<td>920 mAh g⁻¹ after 50 cycles (0.1 Ag⁻¹)</td>
<td>[127]</td>
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<td>Co-assembly</td>
<td>—</td>
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<td>1624 mAh g⁻¹ (0.2 Ag⁻¹)</td>
<td>890 mAh g⁻¹ (5.0 Ag⁻¹)</td>
<td>1026 mAh g⁻¹ after 100 cycles (1.0 Ag⁻¹)</td>
<td>[128]</td>
<td></td>
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<td>Flower-like nanosheets</td>
<td>g~84.3% (1st) &gt;93% (2nd)</td>
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<td>390 mAh g⁻¹ (3.0 Ag⁻¹)</td>
<td>467.3 mAh g⁻¹ after 100 cycles (1.0 Ag⁻¹)</td>
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<td>SnO₂/Cu hybrid nanosheets</td>
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<td>g~98% (2nd)</td>
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<td>535 mAh g⁻¹ after 150 cycles (0.2 Ag⁻¹)</td>
<td>[130]</td>
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<td>Edge/surface functionalization</td>
<td>Fluorinated graphene</td>
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<td>T: ~10 nm</td>
<td>&gt;1000 mAh g⁻¹ (0.05 A g⁻¹)</td>
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<td>780 mAh g⁻¹ after 50 cycles (0.05 A g⁻¹)</td>
<td>[138]</td>
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<td>Fluorographene</td>
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<td>Halogenated graphene nanoplatelets</td>
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<td>SSA: 736.8 m² g⁻¹ EC: 2.201 x 10⁻⁴ cm⁻²</td>
<td>56.2% (1st)</td>
<td>1783.6 mAh g⁻¹ (0.1 C)</td>
<td>~150 mAh g⁻¹ (10 C)</td>
<td>458.0 mAh g⁻¹ after 500 cycles (0.5 C)</td>
<td>[142]</td>
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<tr>
<td>Fluorinated graphene nanoplatelets</td>
<td>Ball-milling</td>
<td>SSA: 134.79 m² g⁻¹ F: 3.0-3.4 at%</td>
<td>66.2% (1st)</td>
<td>1778.1 mAh g⁻¹ (0.1 C)</td>
<td>~200 mAh g⁻¹ (10 C)</td>
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<td>[144]</td>
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<tr>
<td>Nitrogen-doped graphene</td>
<td>CVD</td>
<td>—</td>
<td>—</td>
<td>0.25 mAh cm⁻² (5 μA cm⁻²) ~0.03 mAh cm⁻² (100 μA cm⁻²)</td>
<td>~0.05 mAh cm⁻² after 50 cycles (5 μA cm⁻²)</td>
<td>—</td>
<td>[145]</td>
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<td>Heat treatment</td>
<td>N: 2%</td>
<td>—</td>
<td>&gt;800 mAh g⁻¹ (0.042 A g⁻¹)</td>
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<td>—</td>
<td>[146]</td>
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<td>Nitrogen and fluorine co-doped graphene</td>
<td>Hydrothermal</td>
<td>N: 1.75–3.3 at% F: 1.36–10.9 at%</td>
<td>56.7% (1st) 94% (2nd)</td>
<td>1894 mAh g⁻¹ (0.1 Ag⁻¹)</td>
<td>305 mAh g⁻¹ (5.0 Ag⁻¹)</td>
<td>295 mAh g⁻¹ after 2000 cycles (5.0 Ag⁻¹)</td>
<td>[147]</td>
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<td>79.1% (1st)</td>
<td>94.16 mA h g⁻¹ (0.1 A g⁻¹)</td>
<td>507.6 mA h g⁻¹ (2.0 A g⁻¹)</td>
<td>803.3 mA h g⁻¹ after 100 cycles (0.1 A g⁻¹)</td>
<td>[160]</td>
<td></td>
</tr>
<tr>
<td>MoS₂ hybrid</td>
<td></td>
<td>2D sandwich-like</td>
<td>94.1% (2nd)</td>
<td>~99% (7th)</td>
<td>507.6 mA h g⁻¹ (2.0 A g⁻¹)</td>
<td>803.3 mA h g⁻¹ after 100 cycles (0.1 A g⁻¹)</td>
<td>[160]</td>
<td></td>
</tr>
<tr>
<td>Porous graphene networks</td>
<td>CVD</td>
<td>SSA: 1654 m² g⁻¹</td>
<td>1723 mA h g⁻¹ (0.1 C)</td>
<td>203 mA h g⁻¹ (0.2 C)</td>
<td>391 mA h g⁻¹ (0.4 C)</td>
<td>1043 mA h g⁻¹ after 80 cycles (0.2 C)</td>
<td>[175]</td>
<td></td>
</tr>
<tr>
<td>Mesoporous NiO nanosheet</td>
<td>Solvothermal</td>
<td>T: ~10 nm</td>
<td>878 mA h g⁻¹ (0.2 C)</td>
<td>305 mA h g⁻¹ (1.0 C)</td>
<td>1043 mA h g⁻¹ after 80 cycles (0.2 C)</td>
<td>1043 mA h g⁻¹ after 80 cycles (0.2 C)</td>
<td>[175]</td>
<td></td>
</tr>
<tr>
<td>Mesoporous Co₃O₄ nanosheet</td>
<td>Wet chemical method</td>
<td>T: ~10 nm</td>
<td>5.0 mA h cm⁻² (0.2 C; 0.74 mA cm⁻²)</td>
<td>1.61 mA h cm⁻² (7.38 mA cm⁻²)</td>
<td>330 mA h g⁻¹ after 200 cycles (0.74 mA cm⁻²)</td>
<td>1043 mA h g⁻¹ after 80 cycles (0.2 C)</td>
<td>[175]</td>
<td></td>
</tr>
<tr>
<td>Mesoporous hexagonal Co₃O₄</td>
<td>Annealing</td>
<td>SSA: 189.9 m² g⁻¹</td>
<td>2235 mA h g⁻¹ (0.05 C)</td>
<td>1203 mA h g⁻¹ (0.1 C)</td>
<td>1203 mA h g⁻¹ (0.1 C)</td>
<td>1203 mA h g⁻¹ (0.1 C)</td>
<td>[175]</td>
<td></td>
</tr>
<tr>
<td>N-doped MoS₂ nanosheets</td>
<td>Thermal treatment</td>
<td>SSA: 110.5 m² g⁻¹</td>
<td>99.5% (2nd)</td>
<td>973.2 mA h g⁻¹ (0.05 A g⁻¹)</td>
<td>610 mA h g⁻¹ (2.0 A g⁻¹)</td>
<td>998.0 mA h g⁻¹ after 100 cycles (0.05 A g⁻¹)</td>
<td>[175]</td>
<td></td>
</tr>
<tr>
<td>Hierarchical porous α-Fe₂O₃ nanosheets</td>
<td>Hydrothermal &amp; annealing</td>
<td>SSA: 16.1 m² g⁻¹</td>
<td>68.9% (1st)</td>
<td>1869.3 mA h g⁻¹ (1.006 A g⁻¹)</td>
<td>433.2 mA h g⁻¹ (20.1 A g⁻¹)</td>
<td>877.7 mA h g⁻¹ after 1000 cycles (2.01 A g⁻¹)</td>
<td>[183]</td>
<td></td>
</tr>
<tr>
<td>Hierarchical MoS₂ hollow nanospheres</td>
<td>Solvothermal &amp; heat treatment</td>
<td>SSA: 31.5 m² g⁻¹</td>
<td>83% (1st)</td>
<td>1270 mA h g⁻¹ (0.5 A g⁻¹)</td>
<td>576 mA h g⁻¹ (5.0 A g⁻¹)</td>
<td>1100 mA h g⁻¹ after 100 cycles (0.5 A g⁻¹)</td>
<td>[184]</td>
<td></td>
</tr>
<tr>
<td>Carbon-coated hierarchical SnO₂</td>
<td>Hydrothermal &amp; calcination</td>
<td>SSA: 55.9 m² g⁻¹</td>
<td>98.2% (50th)</td>
<td>1486.7 mA h g⁻¹ (0.1 A g⁻¹)</td>
<td>669.9 mA h g⁻¹ (2.0 A g⁻¹)</td>
<td>900 mA h g⁻¹ after 50 cycles (0.1 A g⁻¹)</td>
<td>[185]</td>
<td></td>
</tr>
<tr>
<td>hollow spheres</td>
<td></td>
<td>Carbon T: ~140 nm</td>
<td>—</td>
<td>1370 mA h g⁻¹ (0.5 C)</td>
<td>510 mA h g⁻¹ (10 C)</td>
<td>860 mA h g⁻¹ after 100 cycles (1 C)</td>
<td>[186]</td>
<td></td>
</tr>
<tr>
<td>Sulfur-impregnated, sandwich-type, hybrid carbon nanosheets</td>
<td>Double template</td>
<td>Carbon T: ~10-25 nm; SSA: 1588 m² g⁻¹ - S: 74 wt%</td>
<td>—</td>
<td>1370 mA h g⁻¹ (0.5 C)</td>
<td>510 mA h g⁻¹ (10 C)</td>
<td>860 mA h g⁻¹ after 100 cycles (1 C)</td>
<td>[186]</td>
<td></td>
</tr>
<tr>
<td>3D V₂O₅/NaV₂O₅/15 hierarchical heterostructures</td>
<td>Gradient hydrothermal</td>
<td>V₂O₅: T: ~100 nm</td>
<td>—</td>
<td>~140 mA h g⁻¹ (0.1 A g⁻¹)</td>
<td>~90 mA h g⁻¹ (5.0 A g⁻¹)</td>
<td>92% retention after 1000 cycles (5.0 A g⁻¹)</td>
<td>[187]</td>
<td></td>
</tr>
</tbody>
</table>

*T, SSA, EC and ID represent the thickness of nanosheets, the largest specific surface area based on the BET method, the electronic conductivity and the interlayer distance of lamellar structures, respectively. Full names of the other abbreviations are as follows: nitrogen-doped graphene (NG), carbon nanofibers (CNFs), carbon nanotubes (CNTs) and chemical vapor deposition (CVD).
In conclusion, the structure optimization strategy, including thickness regulation, porosity manipulation and morphology modulation, offers brilliant opportunities to take full advantage of the merits of the 2D nanostructure. By refining the surface morphology and the structure of the hierarchical nanostructures, the self-aggregation trends of 2D nanosheets can be greatly curbed and the electrochemical reaction between electrolytes and the active materials can be accelerated with a high kinetics. The 3D hierarchical nanostructures with 2D constituents have the features of more active sites, good contact interface and inhibited volume changes, and thus help to improve the maneuverability and practicality of next-generation LIBs.

CONCLUSION AND OUTLOOK

In summary, the distinctive characteristics of 2D nanosheets derived from the unique structure, such as atomic-level thickness, ultrahigh surface area and significant confinement effect, make them promising as electrode materials for LIBs. The grand challenges of the 2D nanomaterials, enhancing the initial Coulombic efficiency, rate capability and cycling stability, however, have greatly restricted their practical applications in batteries, owing to the easy restacking of 2D nanomaterials, the low electrical conductivity of metal oxide and dichalcogenide nanosheets, the obvious volume changes during electrochemical reactions, etc. In this review, three effective strategies are clearly proposed to address these critical issues, including hybridization with conductive substrates, edges/surface functionalization and structure optimization, which can improve the electronic conductivity or/and ion transport, maintain the structural stability of both the 2D nanomaterials and the electrode, and thus promote the lithium-storage capability, rate performance and cycling stability. Table 1 gives a summary of the fabrication methods, the structural parameters and the electrochemical performance (e.g. Coulombic efficiency, rate capability, cycling stability, etc.) of some representative 2D nanomaterials successfully applied with these strategies.

Among these strategies, 2D hybrid nanomaterials consisting of sheet-like TMO or TMD nanomaterials with different conductive materials are easy to obtain by some simple approaches, such as physical mixing, in-situ growth, self-assembly, etc. It is noteworthy that direct coating of nano-carbon on nanosheets is an attractive approach due to the wide range of low-cost carbon sources and the possibility of large-scale production.

The fundamental underlying principle for the strategy of surface/edge functionalization is to alter the electronic properties or the interlayer spacing of the lamellar structures to enhance their electrochemical properties. Accurate control of the doping level and the homogenous formation of atomic-scale defects on the desired locations, however, are relatively difficult to achieve, however, via traditional hydrothermal or thermal treatment routes.

Structure optimization, including thickness regulation, porosity manipulation and morphology modulation, is a further regulation of the surface morphology and the structure of 2D nanomaterials. The hierarchically porous structures assembled from sheet-like 2D building units, which possess the merits of more exposed active sites, shorter diffusion pathways, and better contact between electrolytes and active materials, have great potential for high-performance electrode materials for LIBs.

Very recently, the ingenious combination of two or more of the above proposed strategies, such as the design of hierarchically assembled metal oxide nanosheets hybridized with heteroatom-doped graphene, featuring higher electrical conductivity and chemical reactivity, has offered the potential to make the full use of the advantages of these strategies to achieve possible practical applications. It is therefore believed that these effective strategies for improving the lithium storage of 2D nanomaterials will be good reference points for scientists and researchers in the related fields of materials, chemistry and nanotechnology, who are looking forward to developing superior next-generation rechargeable batteries.

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