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# Hierarchical Structures Based on Two-Dimensional Nanomaterials for Rechargeable Lithium Batteries

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Two-dimensional (2D) nanomaterials (i.e., graphene and its derivatives, transition metal oxides and transition metal dichalcogenides) are receiving a lot attention in energy storage application because of their unprecedented properties and great diversities. However, their re-stacking or aggregation during the electrode fabrication process has greatly hindered their further developments and applications in rechargeable lithium batteries. Recently, rationally designed hierarchical structures based on 2D nanomaterials have emerged as promising candidates in rechargeable lithium battery applications. Numerous synthetic strategies have been developed to obtain hierarchical structures and high-performance energy storage devices based on these hierarchical structure have been realized. This review summarizes the synthesis and characteristics of three styles of hierarchical architecture, namely three-dimensional (3D) porous network nanostructures, hollow nanostructures and self-supported nanoarrays, presents the representative applications of hierarchical structured nanomaterials as functional materials for lithium ion batteries, lithium-sulfur batteries and lithiumoxygen batteries, meanwhile sheds light particularly on the relationship between structure engineering and improved electrochemical performance; and provides the existing challenges and the perspectives for this fast emerging field.

# 1. Introduction

Currently, energy crisis and environmental pollution are recognized as two major challenges to human beings. The continual development of renewable and clean energy sources is critically important for realizing an energy requirement, which is compatible with the goal of sustainable mankind development. For this purpose, high-performance energy conversion and storage devices are needed to enable efficient, versatile, and environmentally friendly uses of energy including electricity.

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Among energy storage systems, rechargeable lithium batteries (RLBs) (e.g., Lithium-ion batteries (LIBs), Lithium-sulfur (Li-S) and Lithium-oxygen (Li-O2) batteries) have drawn consideration attention during recent years due to their superior comprehensive battery performance, compared with lead-acid, Ni-Cd and Ni-MH battery.<sup>[1-3]</sup> However, like the previous battery techniques, its development has also experienced a bottleneck recently. The conventional LIBs are restricted by their theoretical specific capacity and structure stability, making it difficult to further improve their energy density.<sup>[4–6]</sup> Moreover, advanced lithium batteries such as Li-S and Li-O<sub>2</sub> batteries are still studied in their embryonic stages of research and all suffered from several obstacles, for instance, poor utilization of Li metal, high cost, safety concerns, complicated chemical reaction mechanism, poor cycling performance and rate capability.<sup>[7-15]</sup> To meet the ever-increasing demand for high perfor-

mance electric devices, such as power consumer devices (smart phones, laptops, tablets, etc.) and emerging electrical/hybrid vehicles, it is imperative to design and fabricate functional structured electrode materials that provide a high energy density (energy per unit volume) and specific energy (energy per unit mass).

Generally, the materials dimensionality can be categorized into zero-dimensional (0D), one-dimensional (1D) and twodimensional (2D) morphologies. Different-dimensional structures exhibit their unique performances based on surface and structural characteristics.<sup>[16-19]</sup> For example, 0D structured nanoparticles possess shorter the diffusion length and larger electrolyte-electrode contact area compared with the micro-sized particles. However, the aggregation of nanoparticles usually leads to poor electrochemical active. 1D structured nanotubes/ nanowires/nanorods exhibit fast electron transport along the 1D direction, short ion diffusion length along the radial direction. However, their nonadjustable specific surface area and porosity properties limit the scope of application. Beyond 0D and 1D nanomaterials, 2D structured nanosheets/nanoplates/ nanowalls provide greater opportunities for RLBs applications. First, the wide interlayer spacing between nanosheets and their natural electronic properties of eye-catching 2D nanomaterials, e.g., the zero band gap semiconductor graphene and its derivatives, metallic 1T-phase transition metal dichalcogenides (TMDs) and some metallic metal carbides (Mxenes), favor a fast ion and electron transfer, rendering them appealing candidates

for electronic device applications, especially fast charging devices.<sup>[20-23]</sup> Second, the large surface-to-volume ratio endows them with more effectively active sites, making them highly favorable for surface-active applications.<sup>[23]</sup> Last, the atomic thickness offers them good mechanical flexibility, making them suitable for the development of thin, flexible and stretchable batteries.<sup>[23]</sup> However, an enormous challenge of most of 2D nanomaterials is the aggregation or re-stacking of nanosheets, which extremely impedes full utilization of surface area even blocks electrolyte access. One effective way to conquer this obstacle is to construct hierarchical structures. These constructed hierarchical structures using 2D nanomaterials as building blocks not only maintain the intrinsic properties of 2D nanostructures but also exhibit other structural features at different size scales, including large dimensions, accessible porous systems, large void spaces and extraordinary surface area. Based on these unique structural features, the introduction of hierarchical structure composed of 2D nanomaterials shows promising prospects for RLBs electrode. Figure 1 presents the representatively hierarchical structure based on attractive 2D nanomaterials, such as graphene and its derivatives, transition metal oxides (TMOs) and transition metal dichalcogenides (TMDs) and their potential application in non-aqueous LIBs, Li-S and Li-O<sub>2</sub> battery systems.

To date, many research groups have previously reported several review articles on the application of 2D nanomaterials.<sup>[21,24-31]</sup> In this review, we mainly focus on the assemble methods and structure properties of different hierarchical structures of 2D nanomaterials and their promising applications and future opportunities in RLBs. For the description of synthesis approach, the hierarchical structures of 2D nanomaterials are categorized by their structures: three-dimensional (3D) porous network structures, hollow nanostructures and self-supported nanoarrays. For their application, we elucidate their exceptional structural features, general design rules and potential application for energy storage devices including LIBs, Li-S and Li-O<sub>2</sub> batteries, and their current limitations and future research directions.

# 2. Structural Hierarchy Concepts and Their Representative Architecture Based on 2D Nanomaterial

Various types of hierarchical patterns have been observed in many fields, such as ecological systems, nature systems and materials structure systems. The structural hierarchy describes a very specific arrangement of material entities with functional subunits. These subunits have to be possessed individual structure, and organized at different length scale to form a hierarchical structure. As a result, unusual properties of hierarchical structure were obtained, which can outperform their individual structural subunits. The most prominent hierarchical structured sample in nature is the tree, which presented four hierarchical orders: tree, branches, leaves and leaf cells. Similar hierarchical pattern can be applied to construct the advanced architecture for battery electrode materials. A detailed schematic illustration is given in **Figure 2**.





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Most hierarchical structures can be assembled from 0D, 1D, or 2D nanostructures by controlling the experimental conditions.<sup>[19]</sup> The constructed hierarchical structures using 0D/1D/2D nanomaterials as building blocks possess the combined performances of the primary and secondary structures. Thus, the hierarchitectures properties are greatly dependent on





**Figure 1.** Schematic illustration of the hierarchical structure based on 2D nanomaterials and their potential application in various energy storage devices.

the nature of architectonic blocks. Previous studies have demonstrated that the electrode materials with 2D nanostructure to some extent improve the thermodynamics and kinetics of electrochemical reactions. In most cases, 2D nanomaterials with large surface-to-volume ratio can increase the utilization of the active materials and initiate new lithium storage space such as surface/interface and edges, leading to higher specific capacity than 0D and 1D nanomaterials. Besides, their ultrathin thickness can shorten the electrical transport and ionic diffusion distance, and thus will achieve the high power density (rate performance) of the batteries. Moreover, the atomic thickness offers them high mechanical strength as well as high flexibility, minimizing or eliminating the volume change of electrode materials during charging/discharging cycling. Thus, 2D nanomaterials with these unique structural features and outstanding properties are also the ideal building blocks for constructing hierarchical structures. Recently, tremendous progresses have been made in constructing and applying hierarchitectured electrode materials for energy storage devices. Generally, this progress in hierarchitectures constructed by using 2D nanomaterials can be categorized into three groups: (1) 3D porous network structure; (2) hollow nanostructured; and (3) self-supported nanoarrays.

3D porous network structure commonly displays disordered macroporous network, sheet-like structured units constructed by layered 2D nanomaterials. Such structural features



**Figure 2.** Schematic illustration of structural hierarchy of representative architecture assembled from 2D nanomaterials (with the example of MoS<sub>2</sub> aerogels (Reproduced with permission.<sup>[32]</sup> Copyright 2015, American Chemistry Society), MoS<sub>2</sub> hollow sphere (Reproduced with permission.<sup>[33]</sup> Copyright 2014, Wiley-VCH Verlag GmbH&Co.KGaA, Weinheim), and MoS<sub>2</sub> nanosheets arrays on CC substrate (Reproduced with permission.<sup>[34]</sup> Copyright 2014, Royal Society of Chemistry), and structural hierarchy of tree in nature.

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at different length scales impart specific characteristics and properties, such as ultra-light weight, large surface area, high porosity, and stable mechanical strength. This type of hierarchical structure have been extensively applied in popular 2D nanomaterials. Typically, 3D porous network structured graphene and its derivatives have been reported in many field of energy storage devices, sensing, electronics and environment application.<sup>[35]</sup> From the point of energy storage devices, the resulting 3D macro-structures (e.g., graphene foams (GFs),[36-41] graphene aerogels(GAs),<sup>[42-62]</sup> graphene sponges(GSs)<sup>[63-65]</sup> and etc.<sup>[66-70]</sup>) are self-supporting and substrate-free with extraordinary surface area, electronic properties, and chemical activity, allowing the construction of substrate-free electrode for RLBs. Moreover, 3D graphene frameworks with different macroscaled shapes, outstanding electrical conductivity, large surface areas, and high porosity are ideal scaffolds for the loading of various active substances, such as metals, transition metal compounds, and polymers, which enrich their functionalities and broaden the possibilities for their practical application. For instance, Ren et al. fabricated a GFs-rGO (reduced graphene oxides) /S cathode with high sulfur loading of 9.8 mg cm<sup>-2</sup>, showing a high electrical conductivity of 2.64 S cm<sup>-1</sup>, which is almost 23 order of magnitude higher than pure S powders.<sup>[40]</sup> Aside from the graphene and its derivatives, 3D porous network structure of 2D TMOs/TMDs have also been synthesized through different techniques, then possessing the light-weight, high porosity and large specific areas as well. Unlike 3D graphene frameworks, the 3D porous network structure of 2D TMOs/TMDs have not been widely reported in the application of high-performance battery, which may be because of their inferior electrical conductivity and less mature fabrication techniques. One effective way to mitigate these problems is to fabricate hybrid materials by incorporating graphene sheets into the 3D porous network structures. For example, Zeng et al. fabricated 3D porous MoS<sub>2</sub>/graphene hybrid aerogels electrode by a facile hydrothermal self-assembly process.<sup>[59]</sup> The heterostructured MoS<sub>2</sub>-graphene hybrid aerogels exhibited maximal structural compatibility and strong interaction between MoS2 and graphene nanosheets mainly due to the analogous microstructure and morphology between monolayer MoS<sub>2</sub> and graphene nanosheets. Based on the states above, the 3D porous network structures of various 2D nanomaterials provide many outstanding advantages in application, and these will be described in greater detail in section 4.

Compared to the 3D porous network structure, hollow structured 2D nanomaterials typically possesses distinguishable interior void and porous shell, resulting in a lower density and enough space to allow for volume expansion and shorter transport lengths for both mass and charge transport. Hollow structures have received intensive attention as suitable architecture for TMOs/TMDs with sluggish ion/electron transport kinetics and severe volumetric expansion/contraction during the cycling process. This type of hierarchical structure is so far applicable to many TMOs/TMDs with various shapes, such as Fe<sub>3</sub>O<sub>4</sub> hollow sphere,<sup>[71]</sup> TiO<sub>2</sub> hollow tubular,<sup>[72]</sup> MoS<sub>2</sub> hollow tubular,<sup>[73]</sup> MoS<sub>2</sub> hollow box.<sup>[74]</sup> As electrode materials for LIBs, these hollow structured TMOs/TMDs provide outstanding lithium storage performance, compared with their corresponding bulk materials. It is worth reminding that the excess empty space greatly ADVANCED SCIENCE NEWS www.advancedsciencenews.com

reduces tap density, resulting in low volumetric energy and power density of electrode fabricated from these single-shelled materials. Recently, enormous efforts have been devoted to fabricate complex hollow structured TMOs/TMDs (e.g., yolkshelled TiO<sub>2</sub> sphere,<sup>[75]</sup> yolk-shelled δ-MnO<sub>2</sub> sphere,<sup>[76]</sup> multishelled NiS nanobox<sup>[77]</sup> and yolk-shelled MoSe<sub>2</sub> microsphere<sup>[78]</sup>) by advanced synthetic approaches. This strategy represents a promising direction for energy storage devices, not only with higher specific energy density but also with higher specific power density. Apart from the TMOs/TMDs, some hollow structured polynary TMOs/TMDs (e.g., CoMn<sub>2</sub>O<sub>4</sub> hollow sphere,<sup>[79]</sup> Graphene-encapsulated ZnNiCoO microsphere,<sup>[80]</sup> M-Mn based oxides hollow tubular,<sup>[81]</sup> core-shelled NiCo<sub>2</sub>O<sub>4</sub> hollow sphere,<sup>[82]</sup> multi-shelled NiCo<sub>2</sub>S<sub>4</sub> hollow sphere<sup>[83]</sup>) were also attractive electrode materials for LIBs and Li-O2 batteries and etc. Compared to single active component, the hollow structured multi-components present superior electrochemical performance due to their synergetic effect of each component. Additionally, hollow structured graphene and its derivatives with various shapes have also been designed and synthesized to improve the kinetics and electrocatalytic activity of electrode for RLBs.<sup>[84-86]</sup> As a typical example, N-doped graphene/graphene-tube nanocomposites as Li-O<sub>2</sub> battery cathodes exhibited superior oxygen reduction reactions/oxygen evolution reactions (ORR/OER) activity and improved cathode performance compared to traditional carbon black and Pt/C catalysts.<sup>[86]</sup>

Hierarchical structured arrays refer to various dimensional materials comprising 2D building blocks vertically grown on 2D/3D conductive substrate, which can directly serve as self-supported electrode without electrode additives and the additional step of slurry casting during electrode fabrication. Moreover, the direct contact between active materials and the surface of conductive substrate allows for rapid electron collection and transportation to outer circuit. Vertically aligned arrays interconnect each other and produces a large amount of void, offering sufficient space to relieve the structural strain and drastic volume change during lithiation/delithiation. Compared randomly oriented graphene of 3D porous network structure and hollow structure, vertical oriented graphene arrays own many unique features, such as vertical interconnection with the substrate, high surface-to-volume ratio, open channels between the sheets and exposed ultra-thin and ultra-long edges, which will allow a wide range of applications including energy storage devices, sensors, environment fields and etc. For example, the large accessible surface area, large void spaces and high electrical conductivity can encourage wider use of vertically aligned graphene arrays (VAGAs) as anode materials<sup>[87]</sup> or active substrate carries (e.g., Si-nanoparticles @graphene nanosheets (Si-NPs@GNS),<sup>[88]</sup> GeOx,<sup>[89]</sup> SnO<sub>2</sub>-NPs,<sup>[90]</sup> Sn@G<sup>[91]</sup> and S-NPs<sup>[92]</sup> on VAGAs) in RLBs. Moreover, several self-supported TMOs/ TMDs arrays have been highlighted, as their significant features stated above can improve the LIBs performance. Here, the self-supported TMOs/TMDs arrays were categorized into three categories, namely 1D nanostructured core/shell arrays (e.g., nanowires, nanorods, and nanotube), 2D nanostructured arrays (e.g., nanosheets, nanoflakes, nameplates and nanowalls) and its derivatives arrays (e.g., nanowires on nanosheets and nanosheets on nanosheets) to review their important and recent progress in the fields of LIBs. As the most typical



arrays, 2D nanostructured arrays consisted of 2D TMOs/TMDs building blocks have been prepared, including porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets arrays,<sup>[93]</sup> CoO nanosheets arrays,<sup>[94]</sup> mesoporous MnO<sub>2</sub> nanosheets arrays,<sup>[95]</sup> mesoporous NiO nanosheets arrays,<sup>[96]</sup> porous Co<sub>3</sub>O<sub>4</sub> nanosheets arrays,<sup>[97]</sup> mesoporous CuO nanosheets arrays,<sup>[98]</sup> SnO<sub>2</sub> nanosheets arrays,<sup>[99]</sup> MoS<sub>2</sub> nanosheets arrays,<sup>[34]</sup> NiS nanowalls arrays,<sup>[100]</sup> ReS<sub>2</sub> nanowalls arrays,<sup>[101]</sup> NiCo<sub>2</sub>O<sub>4</sub> nanosheets arrays<sup>[102,103]</sup> Co<sub>x</sub>Mn<sub>3,x</sub>O<sub>2</sub> nanosheets arrays<sup>[104]</sup> and MnCo<sub>2</sub>O<sub>4</sub> nanosheets arrays.<sup>[105]</sup> The obtained nanosheets arrays with unique geometric characteristics can be used as roots to fabricate derivative arrays. For instance, 3D hierarchical porous NiCo2O4 nanosheets-derived nanowire cluster arrays on nickel foam were fabricated and applied as anode for LIBs, showing a good cycling stability and rate capability.<sup>[106]</sup> Moreover, hierarchical 1D nanostructured core/shell arrays based on 2D subunits have also been reported in the fields of high-performance electrochemical energy storage. Generally, hierarchical core/shell arrays composed of two or multi-components can not only effectively utilize all the desired functions of each constituent, but also realize the strong synergistic effect of all the active materials. So far, a variety of hierarchical 1D TMOs core/shell arrays, such as Fe2O3 nanorods core @ NiO nanosheets shell,<sup>[107]</sup> CuO nanowire core @ Co<sub>3</sub>O<sub>4</sub> nanosheets shell,<sup>[108]</sup> TiO<sub>2</sub> nanotubes core @ SnO<sub>2</sub> nanoflakes shell,<sup>[109]</sup> CuO nanowires core @ CoO nanosheets shell,<sup>[110]</sup> Co<sub>3</sub>O<sub>4</sub> nanoneedles core @ MnO<sub>2</sub> nanosheets shell<sup>[111]</sup> and Co3O4 nanowires core @ NiO/C nanosheets shell<sup>[112]</sup> have been fabricated as high-performance anodes for LIBs. However, there are few reports on hierarchical TMDs core-shell arrays as anode for LIBs, which may be partially limited by their fabrication method and inherent characteristics. More detailed construction techniques and electrochemical performance of these published hierarchical arrays will be presented in section 3 and 4.

# 3. Preparation Methods of Hierarchical Structure Based on 2D Nanomaterials

### 3.1. 3D Porous Network Structures

Currently, great efforts have been devoted to the exploration of various kinds of synthetic strategies. In general, the fabrication approach of 3D porous network structure was mainly classified into two categories: template-assisted method and template-free method.

Various 2D nanomaterials have been grown or assembled on the various template, such as foam,<sup>[38,113–117]</sup> sponges,<sup>[64,65,118,119]</sup> aerogels,<sup>[120]</sup> alloy sheet,<sup>[66]</sup> layered double oxide (LDO),<sup>[67,121]</sup> polystyrene (PS) ball,<sup>[62]</sup> silicon (Si) sphere,<sup>[122]</sup> salt,<sup>[123]</sup> emulsion,<sup>[124]</sup> ice template<sup>[125,126]</sup> and etc., to form 3D hierarchical porous network structures. Among them, Ni foam (NF) with a pore size of several hundred micrometers, commonly used as the current collector in energy storage application, has been successfully acted as the catalyst template for preparation 3D porous network structures through chemical vapor deposition (CVD) method. Some studies demonstrated this effective and scalable strategy for the preparation of freestanding GFs with a 3D interconnected network.<sup>[38,115,116]</sup> The 3D network structured graphene exhibited a high electrical conductivity, light weight, high porosity, large surface area, and stable mechanical, thermal, and electrical properties. This result suggests that using NF as a template in the CVD process is the effective alternative to prepare 3D hierarchical porous structures with controllable morphology and universality.

Ice crystals formed during the freezing process has been employed as template to produce 3D porous architectures of different materials. Compared to the 0D (spherical particles) and 1D (i.e., nanowires or nanotubes), 2D nanosheets contribute a lot more to viscosity in their stretched state and the interlinking networks from these 2D nanosheets, which are easier to form a aerogel-like material by controlling freezing temperatures. This freeze-drying process has successfully used to fabricate 3D porous network structures of graphene by immersing graphene oxide (GO) sheets dispersion in liquid nitrogen.<sup>[127]</sup> Very recently, MnO<sub>2</sub> aerogels with ultralow density have also been obtained by the self-assembly of 2D MnO2 nanosheets via an ice-templating approach, achieving a high-purity inorganic aerogel without using any functionalization or stabilization agents.<sup>[125]</sup> The obtained MnO<sub>2</sub> aerogel exhibited extremely low density (as low as 0.53 mg  $\text{cm}^{-3}$ ) and a biomimetic foam structure with interconnected macro-pores after self-assembly process (Figure 3a,b). The successful formation of the aerogel and macro-pore morphology can be attributed to the enhanced van der Waals force between the 2D building blocks that have been more orderly arranged by the squeezing of ice crystals during the freezing process (Figure 3c). As illustrated in Figure 3d, the freeze-thawed sediments from ice-squeezed assembly cannot be re-dispersed into a colloid under the ultrasound-treatment, indicating a stable assembly of MnO<sub>2</sub> aerogels.

Additionally, the utilization of porous metal oxide templates as hard templates has been explored to produce 3D hierarchically porous graphene. Zhang et al. fabricated a hierarchically mesoporous oxide template to form a porous graphene framework (PGF).<sup>[67]</sup> In this unique structure, the small pores were introduced by Kirkendall diffusion during calcination of Mg<sub>2</sub>Zn<sub>0.1</sub>Al-layered double hydroxide (LDH) flakes and large pores were attributed to the evaporation of Zn metal during reduction process. Then, 3D graphene with large mesopores was cast onto metal oxides through facile CVD process. The as-prepared porous graphene framework retained the interconnected 3D architecture after the template-dissolving process (Figure 3e). The transmission electron microscope (TEM) image in Figure 3g shows a hierarchically micro- and mesoporous structures in the graphene assembly, which can be convinced by pore-size distribution data (Figure 3f).

Hydrothermal process as the most commonly template-free method to synthesize 3D porous network structure has been used extensively. As a typical example, holey graphene and its derivatives hydrogels can be prepared by one-pot hydrothermal process with simultaneous  $H_2O_2$ -etching reaction in the graphene sheets.<sup>[43,128,129]</sup> In this strategy, GO sheets were reduced and self-assembled into hydrogels with interconnected 3D macroporous network with the pore sizes ranging from submicrometres to several micrometres and the pore walls consisting of single- or few-layer graphene sheets (**Figure 4**a,b).  $H_2O_2$  partially oxidized and etched the carbon atoms around the more active defective sites of GO, leaving behind





**Figure 3.** a) TEM image and photograph (inset) of the colloidal  $MnO_2$  nanosheets. b) SEM image of the obtained  $MnO_2$  aerogel and photograph of the aerogel standing on a dandelion (inset). c) Schematic diagram demonstrating the growth of ice crystals in the  $MnO_2$  colloid during freezing process. d) Schematic illustration for an ultrasound treatment of spontaneous sediments (left) and ice squeezed assembly (right). Reproduced with permission.<sup>[125]</sup> Copyright 2016, Royal Society of Chemistry. e) Schematic for PGF fabrication. A hierarchically porous oxide flake with small pores induced by Kirkendall diffusion during calcination and large pores attributed to volatile metal evaporation during subsequent reduction was used as a hard template to cast graphene. The PGF with large mesopores was obtained by chemical removal of the oxide template. f) Pore size distributions of the PGF and DTG derived from isothermal adsorption plots. g) TEM images of PGF indicating large mesopores. Reproduced with permission.<sup>[67]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

carbon vacancies, which gradually extended into nanopores (Figure 4c,d).<sup>[128]</sup> Further work by shrinking process, a continuous force was generated by the slow evaporation of trapped water in the graphene foam, which pulled apart the interconnected macropores into highly compacted mesopores and promoted the formation of an open microstructure (Figure 4e).<sup>[43]</sup> As results, highly interconnected 3D holey graphene frameworks (HGF) with high density, unique hierarchical porosity, superior electrical conductivity, and exceptional mechanical flexibility were obtained, which were envisaged to be viable for applications in electrochemistry-related fields.

Moreover, inorganic aerogels are usually formed by extracting the liquid of a gel via critical point drying (CPD) in order that the gel network remains intact. The gel networks were assembled through a sol-gel process, where nanoparticle suspensions were formed and then the nanoparticles were cross-linked into 3D network branches by a suitable gelling agent precursor. Because of these specific cross-linking reactions, the material types of aerogels are very limited. Kong et al. reported a new

methodology to make gels over a much wider range.<sup>[130]</sup> It is noteworthy that the formation of 2D material aerogels (MoS<sub>2</sub>, graphene, and hexagonal boron nitride (h-BN) nanosheet) must well control the homogeneous dispersion of the nanosheet at dilute concentration by introducing planar sodium cholate (SC) as a surfactant. However, the aerogels formed by destabilization normally contained trace amount of impurities as a consequence of an incomplete removal of the surfactant and suffered from reduced performance (e.g., charge transport and thermal stability) due to the residual organics. Hence, an approach to fabricate high-purity inorganic aerogels without using any functionalization or surfactant is needed. Worsley et al. prepared monolithic TMDs aerogels by thermal decomposition of freeze-dired traditional precursors, ammonium thio-metal salts.<sup>[32]</sup> The crucial factor in this method is the choice of precursors, which is both favorable to form an extended 3D network structure during the assembly phase and maintain this form upon drying and chemical conversion to the dichalcogenides product. The author proved that the MoS<sub>2</sub> and WS<sub>2</sub> aerogels





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**Figure 4.** a) A Snapshot showing a free-standing holey graphene framework (HGF). b) SEM image of interior microstructures of HGFs. c) Schematic illustration of the preparation process of HGFs. d) TEM image of holey graphene sheets in HGFs. Reproduced with permission.<sup>[128]</sup> Copyright 2014, Nature Publishing Group. e) Schematic of the shrinking process of holey graphene molith (HGM). First, holey-graphene hydrogel (HGH) was obtained by hydrothermal process. HGH was then shrunk into a rigid monolith by a drying process. HGH was finally prepared by annealing the above product. Reproduced with permission.<sup>[43]</sup> Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. f) Synthesis scheme for MoS<sub>2</sub> and WS<sub>2</sub> aerogels. SEM images of g) MoS<sub>2</sub>, and h) WS<sub>2</sub> aerogels. Reproduced with permission.<sup>[32]</sup> Copyright 2015, American Chemical Society.

could be obtained by straightforward thermal decomposition of the ammonium thiomolybdate (ATM) and ammonium thiotungstate (ATT) at 450 °C in hydrogen, respectively (Figure 4f). The resulting  $MoS_2$  and  $WS_2$  aerogels displayed the sheet-like architectures (Figure 4g,h), extreme low density (0.4% and 0.5% theoretical maximum density of single crystal, respectively) and Young's moduli on the order of graphene aerogels.

## 3.2. Hollow Structures

Currently, a diversity of hierarchical hollow structures with various geometric shapes, such as spherical, tubular and other polyhedron hollow nanostructures, have been extensively investigated. In general, the synthesis approaches of these hollow architectures can be divided into three distinct categories: i template-assisted methods, ii sacrificial-template methods and iii template-free methods.

The template-assisted approach is the most common strategy for the construction of hollow structures, which involves the deposition of desired 2D nanomaterials on the surface of the employed template and the selective removal of the template core either by calcination or by solvent etching. To date, most reported hierarchical hollow structures were the spherical hollow structures that were successfully prepared by utilization of diverse removable templates such as colloidal particles,<sup>[84,85,131,132]</sup> emulsion micelles,<sup>[133]</sup> and gas bubbles.<sup>[134]</sup> The hollow graphene-based spheres (HGSs) were mainly fabricated based on spherical templates. For example, our group prepared a hierarchical HGS, which was fabricated by using uniform SiO<sub>2</sub> spheres as hard templates.<sup>[132]</sup> The synthesis process involved three steps (**Figure 5**a), electrostatic assembly







**Figure 5.** a) Schematic illustration of the fabrication procedure of reduced graphene oxide-based hollow spheres (rGO-sp). The electrostatic attraction results in the self-assembling of PEI and GO on SiO<sub>2</sub> spheres, and the following reduction and etching processes endow the assemblies with a hierarchical hollow structure. b)TEM and HRTEM images of rGO-sp. Reproduced with permission.<sup>[132]</sup> Copyright 2013, Royal Society of Chemistry. d) Schematic illustration of the formation of HTS of Mn-based mixed metal oxides. e) FESEM and f) TEM characterizations of CoMn-HTSs. Reproduced with permission.<sup>[81]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. g) Schematic illustration of the template-assisted formation of hierarchical MoS<sub>2</sub> microboxes. h) FESEM and i) TEM images of hierarchical MoS<sub>2</sub> microboxes. Reproduced with permission.<sup>[74]</sup> Copyright 2014, Royal Society of Chemistry. j) Illustration of the synthesis process of C@MoS<sub>2</sub> nanoboxes. k) SEM and I) TEM images of C@MoS<sub>2</sub> nanoboxes. Reproduced with permission.<sup>[139]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

to obtain the GO coated SiO<sub>2</sub> spheres, Na–NH<sub>3</sub> reduction process to remove oxygen-containing groups and restore graphene structure, and the dissolution of the SiO<sub>2</sub> core by immersing in concentrated hydrofluoric acid. The obtained hollow rGO-based spheres (rGO-sp) remained spherical configuration and had a diameter of 400–500 nm (Figure 5b,c). The high resolution transmission electron microscopy (HRTEM) image in inset of Figure 5c shows typical wrinkles and folds on rGO-sp, and the parallel lines indicate the layered structure formed during the assembly process. Rationally engineered hollow graphenebased nanostructure possessed nanosized hollow interior, interconnected conductivity network and large specific area. Moreover, hierarchical tubular structures (HTSs) have been reported by using one-dimensional nanostructured template, including nanofibers,<sup>[81,135]</sup> nanowires<sup>[72,136]</sup> and nanotubes.<sup>[137,138]</sup> Lou's group demonstrated a general and cost-effective approach to synthesize HTSs of Mn-based (Co-Mn, Ni-Mn, Cu-Mn, and Zn-Mn) mixed metal oxides constructed by nanoflake subunits via using carbon nanofibers (CNFs) as a supporting template<sup>[81]</sup> (Figure 5d). In hydrothermal process, core-shelled CNFs@M-Mn precursor nanocables were synthesized in the presence of M<sup>2+</sup> cations (M = Co, Ni, Cu, and Zn). Due to the strong redox reaction between KMnO<sub>4</sub> and CNFs, the as-formed M-Mn precursor with ultrathin flake-like subunits was grown readily around the CNF surface to form the 1D CNFs@M-Mn precursor core-shell structure. In annealing

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process, the CNFs template was removed through thermal treatment at 500 °C for 2 h in air to form HTSs. FE-SEM and TEM images of CoMn-HTSs samples confirm that the hierarchical shell structure was constructed by flake-like subunits with a thickness of several nanometers (Figure 5e,f). In virtue of the unique structural features, the CoMn-HTSs samples manifested a high Brunauer–Emmett–Teller (BET) specific surface area of 60.8 m<sup>2</sup> g<sup>-1</sup>. Other than 1D nanostructured template, cage-containing metal-organic frameworks (MOFs) have also been employed as templates to produce hierarchical tubular structures, which provided new opportunities in synthesizing efficient ORR catalysts.<sup>[86]</sup>

Hollow nanostructured spheres and tubular structures based on 2D nanomaterials have been extensively prepared by template-assisted approach. However, the synthesis of hollow polyhedron structures is still a great challenge due to the lack of polyhedron templates. Lou's group has successfully realized hierarchical MoS2 microboxes constructed by ultrathin nanosheets, which employed the pre-prepared MnCO<sub>3</sub> microcube as a template (Figure 5g).<sup>[74]</sup> First, uniform MoS<sub>2</sub> nanosheets were grown on MnCO3 microcube templates via an L-cysteine assisted hydrothermal method. Simultaneously, the MnCO<sub>3</sub> precursor was converted to MnS, and then was selectively dissolved in 1 м HCl solution to produce hierarchical MoS<sub>2</sub> microboxes. The SEM and low-magnification TEM image reveal a cubic void inside the microbox (Figure 5h,i). Further high-resolution TEM image clearly elucidates the ultrathin nature of the MoS<sub>2</sub> nanosheets (inset of Figure 5i). In their further work, a unique hybrid hollow structure by growing ultrathin MoS<sub>2</sub> nanosheets on N-doped carbon shells (denoted as C@MoS<sub>2</sub> nanoboxes) was designed and synthesized by using pre-prepared Fe<sub>2</sub>O<sub>3</sub> nanocubes as the template.<sup>[139]</sup> The N-doped carbon shells can greatly improve the conductivity of the hybrid structure and effectively prevent the aggregation of MoS<sub>2</sub> nanosheets. The synthesized processes are presented in Figure 5j. The Fe<sub>2</sub>O<sub>3</sub> nanocubes were firstly coated with a uniform and smooth carbon layer of polydopamine (PDA). After carbonization in N<sub>2</sub>, the obtained Fe<sub>3</sub>O<sub>4</sub> core can be easily dissolved by HCl to achieve hollow carbon nanoboxes. The resulting C@MoS<sub>2</sub> nanoboxes perfectly exhibited the nanosheets-on-box nanostructure, and each  $MoS_2$  nanosheet was composed of three to five layers only (Figure 5k,l). Based on the above observations, the template-assisted method is the very straightforward and effective method to accurately obtain the size and shape of the designed hollow structures. However, the templates removal process requires special care as deformation and collapse of the shells will otherwise occur. On the other hand, the synthesis of the non-spherical hierarchical hollow structures and complex hollow structures (e.g., yolk-shelled and multi-shelled) by template-assisted method still faces a major challenge to find the right chemistry for deposition of designed materials on the appropriate templates that can be selectively removed. Therefore, it is urgent to develop novel approaches to prepare hierarchical hollow micro/nanostructures.

The sacrificial-template approaches involving fantastic mechanisms such as self-templating,<sup>[71,77,83,140]</sup> chemical oxidation reaction,<sup>[76]</sup> thermal decomposition,<sup>[33]</sup> ion-exchange reaction<sup>[78,141,142]</sup> and kirkendall effects<sup>[143]</sup> have demonstrated their feasibility and effectiveness to prepare high-quality hierarchical

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hollow structures with distinct morphologies and compositions. For instance, Qian and co-workers developed a hollow  $MoS_2@C$  nanotube using a simple hydrothermal sulfuration of  $Mo_3O_{10}(C_2H_{10}N_2)$  nanowire method along with glucose carbonization, which can be explained by the nanoscale Kirkendall effect.<sup>[143]</sup> With increasing the reaction time, the XRD diffraction peaks of  $Mo_3O_{10}(C_2H_{10}N_2)$  were weakened; in the meantime, the peak intensity of  $MoS_2$  increased, suggesting that  $Mo_3O_{10}(C_2H_{10}N_2)$  was transformed to  $MoS_2$  continuously (**Figure 6**a,b). The TEM image indicates that the central part of nanowire gradually became transparent and some nanosheets emerged on the surface of the nanowires leading to a rough edge as the reaction time increasing.

Apart from single-shelled hollow structure, sacrificial-template approach can easily obtained multi-shelled hollow structured 2D nanomaterials. For instance, Lou's group developed a general self-templating strategy to fabricate hierarchical nickel sulfide (NiS) box-in-box hollow structures.<sup>[77]</sup> Firstly, Silica (SiO<sub>2</sub>) nanoboxes were acted as the self-sacrificial template to synthesize nickel silicate box-in-box hollow structures by a simple hydrothermal method. Then, the as-prepared nickel silicate structure can be converted into NiS box-in-box hollow nanostructures through a solution-based sulfidation method (Figure 6c). The FESEM and TEM images show that the NiS sample displayed a unique ball-in-ball hollow structure (Figure 6d,e). A higher magnification TEM image reveals that the shell of NiS was composed of ultrathin nanosheets (Figure 6f). Due to the unique box-in-box hollow structure and ultrathin nanosheets, the obtained NiS samples possessed a relatively high BET surface area of about 140.28  $m^2 g^{-1}$  and a high pore volume of  $0.3 \text{ cm}^3 \text{ g}^{-1}$ . This sacrificial-template method exhibited the similar merits of the template-assisted methods. More importantly, the pre-grown templates in this strategy can be fabricated and then self-depleted during the synthetic process.

Moreover, much effort is also being devoted to establishing template-free method, by the Ostwald ripening<sup>[82,144-146]</sup> and chemically induced self-assembly<sup>[73,75,79,147]</sup> to synthesize hierarchical hollow structure in a cost-effective and high-output way. This approach usually involved aggregation of nanocrystals to a spherical or other morphologies to reduce the high surface energy of the newly formed small crystallites, followed by dissolution of the crystallites inside space and recrystallization at the surface, thus giving rise to special hollow or multi-shell structures. For instance, Chen et al. presented hierarchical NiCo2O4 core-void-shell microspheres composed of porous nanosheets by a facile hydrothermal process and followed by a calcination process.<sup>[82]</sup> Based on the change of morphologies during hydrothermal process, the main driving force for the formation of core-void-shell structure was the inside-out Ostwald ripening (Figure 7a,b). As results, the microspheres with a core-void-shell structure were constructed by 10-nm-thick nanoplates as shown in TEM (Figure 7c). Moreover, the small pores can be clearly seen on the surface of the nanoplates, which were related to the release of gas during the crystal transformation at 450 °C (inset of Figure 7c). The template-free method has also been explored to synthesize hierarchical hollow tubular structures constructed by ultrathin nanosheets. Wang et al. prepared 3D tubular architectures constructed by single-layered MoS<sub>2</sub> via a spontaneous self-assembly process.<sup>[73]</sup> In this case, the dipole-dipole



**Figure 6.** a) XRD patterns of samples obtained from different reaction time. b) TEM images of products obtained at different reaction time from 0 to 12 h. Inset: High-angle annular dark-field STEM image of the MoS<sub>2</sub>@C nanotube. Reproduced with permission.<sup>[143]</sup> Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. c) Schematic illustration for the formation process of the NiS box-in-box hollow structure. d) FESEM and e–f) TEM images of NiS box-in-box hollow structures. Reproduced with permission.<sup>[77]</sup> Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

interactions should be the main driving force for the assembly behavior of semiconductor nanosheets. Owing to their unique structure, the hierarchical  $MoS_2$  nanotubes displayed a high specific area of tubular structures with mesoporous (3 nm). FESEM and TEM images confirm that the resulting materials had tubular morphologies with uniform diameters of about 180–210 nm and a length of 2 µm (Figure 7d,e). A high-resolution TEM image of a tube edge clearly indicates that the tube was indeed composed of  $MoS_2$  nanosheets (Figure 7f,g). Compared to the template methods, template-free method is more simplify and efficient approach in some cases. However, it is extremely difficult to control the uniformity of shape, size and shell thickness using template-free methods.

### 3.3. Self-Supported Nanoarrays

Self-supported nanoarrays have become a rapidly growing field of research in recent years. Large-scale production of

high-quality hierarchical nanoarrays with low-cost and environmental friendly is of great importance for practical application in energy storage advices. The performance of the nanoarray electrodes is largely dependent on the morphology and structure of the hierarchical nanoarrays, which can be easily modulated by adjusting the synthetic method and growth conditions. Till now, diverse methods for the synthesis of hierarchical nanoarrays have been developed in recent years, such as electrochemical deposition (ED) method, solvothermal method, chemical deposition (CD) method, chemical vapor deposition (CVD) and their combinations.

Electrodeposition (ED) provides several advantages in comparison with other methods, like low cost, large-scale deposition and possibility of morphology control of resultant electrode. The shape and the properties of obtained products may be varied by the change of parameters such as the type and concentrations of precursors, temperature, a substrate and method of its pretreatment as well as by manipulation with





**Figure 7.** a) Scheme of reaction process of NiCo<sub>2</sub>O<sub>4</sub> at different reaction times: 1 h, 3 h, 5 h, and 10 h. b) Corresponding TEM images of reaction process. c) Low-magnified FESEM images of porous NiCo<sub>2</sub>O<sub>4</sub> core–shell microspheres. Inset: High-magnified FESEM images of porous NiCo<sub>2</sub>O<sub>4</sub> core–shell microspheres. Inset: High-magnified FESEM images of porous NiCo<sub>2</sub>O<sub>4</sub> core–shell microspheres. Reproduced with permission.<sup>[82]</sup> Copyright 2015, Elsevier. d) SEM and e–f) TEM images of the 3D tube architectures assembled from single-layered MoS<sub>2</sub>. g) Enlarged TEM image of a single MoS<sub>2</sub> tube. The arrows indicate the separated MoS<sub>2</sub> layers with thickness below 0.7 nm. Reproduced with permission.<sup>[73]</sup> Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

electrochemical parameters (current density or electrodeposition potential). As a typical example, Lou et al. prepared a mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanosheets supported on NF by potentiostatic ED technique.<sup>[102]</sup> The electrodeposition was performed in a standard three-electrode glass cell consisting of the clean NF working electrode, a platinum plate counter electrode and a saturated calomel reference electrode (SCE) at a temperature of 10  $\pm$  1 °C. Firstly, the (Ni, Co) hydroxide precursors were electrodeposited on the Ni foam in a 4 mM Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 2 mM Ni(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O aqueous mixed electrolyte at -1.0 V (vs SCE) for 5 min. Then the samples were rinsed with distilled water and annealed at 300 °C for 2 h to form mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanosheets arrays. Due to the inter-linking of large lateral sized nanosheets, the hierarchical porous nanosheets nanoarrays possessed abundant open space and active sites. Moreover, numerous mesopores with a size ranged from 2 to 5 nm in these ultrathin nanosheets were obtained, resulting from the thermal decomposition of the hydroxides. Additionally, galvanostatic ED technique can also be acted as a simple and effective method to prepare ultrathin and highly ordered nanosheet. Wang et al. reported high-quality CoO nanosheet arrays (NSAs), which involved galvanostatic electrodeposition of Co(OH)<sub>2</sub> on the substrate and subsequent thermal transformation to CoO (Figure 8a).<sup>[94]</sup> The obtained CoO NSAs exhibited ultrathin characteristics (8 nm) and the porous structure (2.7 nm) composed of the homogeneous overlapped nanocrystals, which provided enormous opportunities for enhancing

their functions and application performance (Figure 8b,c). Other hierarchical nanosheet nanoarrays have also been realized by potentiostatic or galvanostatic ED and applied for electrochemical energy storage.<sup>[95,97,148–150]</sup>

TMDs nanoarrays were usually obtained from their metal oxide or hydroxide nanoarrays by an ED process and followed by a simple anion exchange reaction. The anion exchange process circumvented the drawbacks of high temperatures, high pressure and toxic sulfur-containing precursor and significantly reduced the fabrication cost while maintaining an excellent reproducibility. Fan and co-workers fabricated CoS nanowall arrays through direct anion exchange reaction from Co<sub>3</sub>O<sub>4</sub> nanowall arrays.<sup>[100]</sup> First, the Co(OH)<sub>2</sub> nanowall arrays were prepared via galvanostatic electrodeposition After annealing in argon, the Co(OH)<sub>2</sub> nanowall arrays could be converted into Co<sub>3</sub>O<sub>4</sub> nanowall arrays. Finally, the CoS nanowall arrays were successfully obtained by placing Co<sub>3</sub>O<sub>4</sub> nanowall arrays in a sealed cup with a solution containing sodium sulfide (Na2S 0.1 M) at 90 °C for 9 h. The anion-exchanged CoS kept the vertical network configuration and the nanowalls exhibited dense pore structure and a rough texture.

Recently, template-assisted ED growth of hierarchical nanoarrays on 3D porous substrate has been emerged.<sup>[151,152]</sup> Typically, the ZnO microrod arrays were the one of the most common template for the fabrication of complex hollow nanorod/nanotube arrays. The electrochemical synthesis from aqueous solution containing  $Zn^{2+}$  ions and source of





**Figure 8.** a) Schematic illustration for the fabrication of CoO NSAs. b) SEM image of CoO NSAs. Inset: Snapshot of CoO array on NF substrate. c) Magnified SEM image of CoO NSAs. The Inset indicates the separated CoO nanosheets with thickness about 10 nm. Reproduced with permission.<sup>[94]</sup> Copyright 2014, Royal Society of Chemistry. d) Schematic illustration of ED-synthesis of hierarchical porous NiO nanotube arrays. e) SEM image of SEM image of hierarchical porous NiO nanotube arrays. g) TEM image of hierarchical porous NiO nanotube arrays. g) TEM image of hierarchical porous NiO nanotube arrays. Reproduced with permission.<sup>[151]</sup> Copyright 2014, Elsevier. h) Fabrication process of 3D hierarchical tubular CuO/CoO core/shell heterostructure arrays on Cu foam. i) Schematic diagram of formation mechanisms of 3D hierarchical tubular CuO/CoO core/shell heterostructure arrays. Reproduced with permission.<sup>[10]</sup> Copyright 2015, Elsevier.

OH<sup>-</sup>, consisted in electroreduction of hydroxide precursor, followed by precipitation of Zn(OH)2 and dehydration to ZnO, was reported by Izaki et al.<sup>[153]</sup> Cao et al. prepared a 3D hierarchical porous NiO nanotube arrays on NF by ED method with the help of pre-made ZnO nanorod template (Figure 8d).<sup>[151]</sup> First, the ZnO microrod arrays as the template were electrodeposited on NF in solution of 0.01 M Zn(NO<sub>3</sub>)<sub>2</sub> and 0.05 M NH<sub>4</sub>NO<sub>3</sub> with current density of 0.25 mA cm<sup>-2</sup> at 70 °C for 45 min. Then, the as-prepared ZnO nanorod arrays were used as the scaffold for NiO nanoflake shell growth via using the ED method again. Finally, the hierarchical porous NiO nanotube arrays were fabricated after dissolving the ZnO nanorod arrays template in a sodium hydroxide solution and annealing in argon. The electrodeposited ZnO nanorod had an average diameter of 60 nm, length up to around 1 mm (Figure 8e). After etching the ZnO template, self-supported NiO nanotubes composed of nanoflakes of about 10 nm thickness were left on the NF substrate (Figure 8f). The TEM shown in Figure 8g suggests that the porous NiO nanotubes comprised of interconnected NiO nanoflakes and showed a tubular structure, indicating a unique hierarchical porous hollow structure.

The term "chemical deposition (CD) method" is used here for techniques that produce hierarchical nanoarrays on substrate in a solution-immersion through control of the kinetics of formation of the nanoarrays. Many hierarchical TMOs/TMDs nanoarrays have been prepared by this technique.<sup>[34,98,100,110,154,155]</sup> For instance, Sun et al. reported hierarchical CuO nanoarrays on a 2D Cu substrate by a facile and low-cost vapor-phase corrosion approach.<sup>[98]</sup> The vapor-phase corrosion approach was realized by the complex chemical reaction of metal Cu and the vapor of ammonia solutions. After that, a blue Co(OH)<sub>2</sub> was heated in N<sub>2</sub> at 180 °C for 2 h to form CuO mesoporous nanosheet cluster. The resultant hierarchical CuO nanoarrays consisted of hierarchically mesoporous CuO nanosheets assembled gearlike pillar arrays, which can be tuned by adjusting the temperature and concentration of ammonia solutions. Later on, Zhang et al. fabricated 3D hierarchical tubular CuO/CoO core/shell heterostructure arrays by two-step chemical precipitation method with the aid of

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 $Co(OH)_2$  nanorod (Figure 8h).<sup>[110]</sup> The Co(OH)<sub>2</sub> as a backbone was firstly prepared by the chemical reaction of Cu foam and alkaline solution (2.5 mol L<sup>-1</sup> sodium hydroxide and 0.1 mol L<sup>-1</sup> ammonium persulphate). Then, the branched cobalt precursor nanosheets obtained through the reaction of Co<sup>2+</sup> with OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> were grown uniformly on the Cu(OH)<sub>2</sub> nanorod backbones by the CD method. As the concentration of NH<sub>4</sub><sup>+</sup> and H<sup>+</sup> in solution increased, the inner Cu(OH)<sub>2</sub> nanorod cores were gradually consumed to create hierarchical tubular Cu(OH)<sub>2</sub>/CoO precursor core/shell arrays. After annealing, 3D hierarchical tubular CuO core/CoO shell arrays were successfully fabricated, and the formation mechanism is illustrated in Figure 8i. It is clearly revealed that CuO possessed hollow interior, and the CoO nanosheets uniformly and closely anchored on the surface of the CuO nanotubes (inset of Figure 8i-(c)).

2D TMDs nanomaterials, such as MoS<sub>2</sub> nanosheet vertically grown on active carbon fiber (ACF) cloth, can be synthesized by CD method as well.<sup>[34]</sup> First, the ACF cloth was immersed into the mixed solution ((NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> in dimethylformamide (DMF)) for 15 min, and dried at 90 °C in a vacuum oven. After that, the MoS<sub>2</sub>/ACF cloth composites were obtain by annealing at 750 °C for 2 h in a 5% H<sub>2</sub>/Ar atmosphere, which exhibited hierarchical porosity and an interconnected framework. In addition, the NiS nanowall arrays on carbon fiber cloth could be fabricated through direct ion exchange from NiO nanowall array prepared via CD method.<sup>[100]</sup> The NiO nanowall arrays were prepared by immersing the mixed solution (ammonia, nickel sulfate and potassium persulfate) for 30 min at 25 °C and then annealing at 200 °C in argon. Finally, NiO nanowall arrays were converted into NiS nanowall arrays in a Na<sub>2</sub>S aqueous solutions. The obtained NiS nanowall arrays maintained the nanowall network architecture of NiO, while the surface of walls became rougher than the pre-forms.

The plasma-enhanced chemical vapor deposition (PECVD) has been emerged as a key method for VAGAs synthesis.<sup>[87,156-159]</sup> By tuning the plasma growth conditions, the VAGAs can be synthesized in a low-temperature, highly-efficient, and catalyst-free manner, with controllable structures and properties. Chen et al. reported the carbon nanowalls synthesis using direct current (dc) PECVD at atmospheric pressure.<sup>[156]</sup> This atmospheric method was capable of producing VAGAs on various substrates (e.g., copper, silicon, stainless steel, carbon nanotubes) at a relatively low cost, thereby showing promise for large-scale applications. Xiao et al. prepared the VAGAs synthesized via microwave plasma enhanced chemical vapor deposition (MW-PECVD).<sup>[87]</sup> The vertically aligned graphene sheets on Ni foil were synthesized directly from gas precursors in a bottom-up growth process, which greatly decreased the possibility of contamination compared to top-down approaches such as oxidation-reduction and ball-milling processes. Recently, Fan et al. proposed a 3D perpendicularly-oriented graphene (POG) grown on all-sides of NF by MW-PECVD process.[159] The NF was firstly pressed to a thickness of about 0.2 mm in order for uniform coating and further etched with H<sub>2</sub> plasmas. Then, the POG/NF electrodes were produced by a MW-PECVD system using methane ( $CH_4$ ) and hydrogen ( $H_2$ ) as source gases. By using of high-purity carbon source gas and a low-pressure plasma process, the oxygen-containing functional groups in POG were lowered. The photograph in Figure 9a shows the contrast of the circular NF electrode before and after POG deposition. After PECVD growth, the POG with height of about 2  $\mu$ m was grown vertically on all sides of NF (Figure 9b,c). Figure 9d clearly exhibits that the graphene nanosheets were interconnected each other, providing hierarchical porous structures.

Moreover, CVD growth of metal sulfide nanosheets or nanowalls on conductive substrates has been reported.<sup>[101,160]</sup> Huang et al. prepared an ultrathin MoS<sub>2</sub> nanosheets vertically aligned on the single layer graphene sheet coated Ti substrate by CVD method.<sup>[160]</sup> As illustrated in Figure 9e, the graphene sheet provided a novel substrate for the nucleation and subsequent growth of MoS<sub>2</sub> nanosheets, which can be attributed to that the boundaries and impurities of graphene sheet could serve as nucleation sites. However, it was difficult to form homogeneous nucleation on bare Ti substrate. Thus, the MoS<sub>2</sub> NPs were formed on Ti substrate when the MoS<sub>2</sub> vapor was supersaturated during the cooling step. The Figure 9f clearly shows the boundary between MoS<sub>2</sub>-NPs/Ti and MoS<sub>2</sub> nanosheets/Graphene. In the area of MoS<sub>2</sub> nanosheets/Graphene, the MoS<sub>2</sub> sheets were vertically aligned on the monolayer graphene sheet. As displayed in Figure 9g, the obtained MoS<sub>2</sub> sheets presented a mesoporous structure, which may be due to the sulfurization of the MoO<sub>3x</sub> via the Kirkendall effect. Although many proof-ofconcept studies have demonstrated the unique merits of CVD approaches, there is no doubt that the CVD growth procedure is complicated and expensive. In addition, the growth mechanism is still not yet well understood.

Among the numerous synthesis methods, solvothermal treatment received wide investigations, owing to their cost-effective, easy route to obtain hierarchical structure, and the feasibility/ availability of widespread applications. Generally, the structure of the products could be tailored by controlling the composition of the solvent used for the solvothermal reaction.<sup>[93,104,105,163]</sup> For instance, hierarchical NiMoO<sub>4</sub> NSAs on various conductive substrate were readily obtained by adjusting the volumetric ratio of ethanol/water in the mixed solvent for solvothermal process.<sup>[163]</sup> After annealing, the obtained NiMoO<sub>4</sub> nanosheet presented mesoporous characteristics, mainly deriving from the recrystallization process and release of gas at high temperature. However if only H<sub>2</sub>O is used as solvent for the solvothermal synthesis, Ni-Mo precursor with rod-like structures would be directly grown on substrates. NH<sub>4</sub>F as a functional agent, was usually used to guide the growth of sheet-like morphology in solvothermal process.<sup>[99,103,106,111,164–166]</sup> For example, Cao et al. explored the formation process of the hierarchical SnO<sub>2</sub> NSAs with NH<sub>4</sub>F in solvothermal synthesis.<sup>[99]</sup> The as-prepared structures were prone to grow 2D nanosheets with the addition of NH₄F. The formation process is illustrated in Figure 9h. At the first stage, the SnO<sub>2</sub> nanocrystals were homogenously grown on NF. With the reaction time increasing, the SnO<sub>2</sub> nanoparticles were directionally aggregated into SnO<sub>2</sub> nanorods (Figure 9i). After a prolonged time, the SnO<sub>2</sub> nanosheets were densely and uniformly deposited on the nickel foam backbone, displaying perfect hierarchical nanoarrays (Figure 9j). Layered CoAl layered double hydroxides (CoAl LDHs) can also be employed as pristine materials to fabricate hierarchical nanosheets arrays (NSAs).<sup>[167]</sup> Firstly, CoAl LDHs NSAs was easily synthesized by a simple homogeneous hydrothermal method. After etching,





**Figure 9.** a) Photographs of bare NF and POG/NF electrode. b) SEM top-views and c) cross-sectional view of POG. d) High-magnified SEM image of POG. Reproduced with permission.<sup>[159]</sup> Copyright 2014, Elsevier. e) Schematic diagram of controlled CVD growth of  $MoS_2$ -NP/Ti and  $MoS_2$ -NS/G. f) FESEM image of the boundary between  $MoS_2$ -NP/Ti and  $MoS_2$ -NS/G. g) TEM image of  $MoS_2$ -NS/G. Reproduced with permission.<sup>[160]</sup> Copyright 2015, Elsevier. h) Schematic illustration of the formation process of the hierarchical  $SnO_2$  NSAs on Ni foam i–j) FESEM images of the samples obtained with different reaction time: j) 3 h and i) 24 h. Reproduced with permission.<sup>[99]</sup> Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. k) SEM image of the hierarchical NiCo<sub>2</sub>S<sub>4</sub> core-shell nanowire arrays after sulfurization for 48 h. Inset: magnified SEM image l) TEM images of the hierarchical NiCo<sub>2</sub>S<sub>4</sub> core-shell nanowire arrays. Reproduced with permission.<sup>[161]</sup> Copyright 2016, Nature Publishing Group. m–n) SEM images of structured Ni<sub>3</sub>S<sub>2</sub> core nanorods@MoS<sub>2</sub> shell nanosheets arrays obtained from different concentration of TAA: m) 1.5 g L<sup>-1</sup>, and n) 2 g L<sup>-1</sup>. Reproduced with permission.<sup>[162]</sup> Copyright 2014, Elsevier.

the uniform 2D Co<sub>3</sub>O<sub>4</sub>-based NSAs was obtained. Then, the Co<sub>3</sub>O<sub>4</sub>@NiMoO<sub>4</sub> NSAs were fabricated by using Co<sub>3</sub>O<sub>4</sub>-based NSAs as building blocks in a typical hydrothermal process. As results, the Co<sub>3</sub>O<sub>4</sub>-based NSAs with numerous holes were wrapped by a randomly oriented NiMoO<sub>4</sub> shell to form a sandwich-like 3D hierarchical architecture.

The hydroxide/oxides precursor nanoarrays obtained via solvothermal synthesis can be easily converted to their hierarchical TMDs nanoarrays by a sulfurization treatment.<sup>[161,168]</sup> Hu et al. prepared hierarchical NiCo<sub>2</sub>S<sub>4</sub> core-shell nanowire arrays on graphene/NF (Ni@G) substrates by this strategy.<sup>[161]</sup> Graphene was pre-coated on NF to protect it which would otherwise become fragile during the sulfurization. During synthetic process, the (Ni, Co) hydroxide nanowire arrays on the surface of Ni@G foam were first prepared by urea-assisted solvothermal process. The NiCo<sub>2</sub>S<sub>4</sub> core-shell nanowires were



obtained after sulfurization treatment process. The obtained NiCo<sub>2</sub>S<sub>4</sub> core nanowires exhibited mesoporous structure, deriving from the replacement of O<sup>2-</sup> by S<sup>2-</sup> through sulfurization process (Figure 9l). As the sulfurization time prolonged to 48 h, it can be clearly seen from Figure 9k that the ultrathin NiCo<sub>2</sub>S<sub>4</sub> nanosheets uniformly enwrapped the porous NiCo<sub>2</sub>S<sub>4</sub> nanowire, forming a core-shell hierarchical and highly porous nanoarrays. The solvothermal process using sulfur-containing solvent was also able to construct hierarchical metal sulfide nanoarrays.  $^{[162,169,170]}$  As an example, hierarchical  $\mathrm{Ni}_3S_2$  core nanorods@MoS2 shell nanosheet nanoarrays were synthesized by one-step solvothermal method using thioacetamide (TAA) as a sulfurization solvent.<sup>[162]</sup> In this solvothermal process, the S2- released from TAA was directly reacted with Ni foam to produce oriented Ni<sub>3</sub>S<sub>2</sub> nanorods. After introducing MoO<sub>4</sub><sup>2-</sup> ions, the MoS<sub>2</sub> nanosheets were obtained and densely grown on Ni<sub>3</sub>S<sub>2</sub> core nanorods. The SEM images in Figure 9m,n suggest that the shell thickness of  $MoS_2$  nanosheet was increased by increasing concentration of the sulfur source. In the future work, solvothermal route still needed to conquer enormous challenges for broad application, including fairly long reaction time, difficulty in scale-up and achieving uniform size.

Till now, it is a pivotal issue to fabricate complex hierarchical nanoarrays with precise structure control by a one-step synthesis method above, which may be due to their complex architectures and chemical compositions. Thus, many researchers proposed multi-step hybrid strategy to synthesize complex hierarchical nanoarrays by combining various methods, such as solvothermal and ED method,<sup>[171-174]</sup> solvothermal and CD method,<sup>[107,112,175-177]</sup> solvothermal and CVD,<sup>[109]</sup> ED and CD method.<sup>[178-180]</sup> As an example, Fan and co-workers presented a two-step synthesis of the Co<sub>3</sub>O<sub>4</sub>/NiO and ZnO/NiO core/shell nanowire arrays by combining solvothermal synthesis and CD methods.<sup>[176]</sup> As illustrated in Figure 10a, self-supported Co<sub>3</sub>O<sub>4</sub> or ZnO nanowire arrays were firstly prepared by a facile solvothermal synthesis method. Then, the obtained metal oxide nanowires were used as the scaffold for NiO nanoflake growth in a simple CD process, forming advanced core/shell nanowire nanoarrays (Figure 10b). The as-prepared NiO shell possessed a 2D sheet-like structure due to their "oriented attachment" and "self-assembly" processes. Based on this principle, the NiO nanosheet obtained by this CD method can also be grown on other backbones to form diverse hierarchical nanoarrays. Duan et al. constructed hierarchical metal sulfide core/shell nanoarrays (CoS core nanowires@NiCo<sub>2</sub>S<sub>4</sub> shell nanosheet) by combining solvothermal, ED process and subsequent ion exchange reaction.<sup>[172]</sup> From the SEM image in Figure 10c, it can be seen that the CoO nanowires were wrapped by the ultrathin NiCo<sub>2</sub>O<sub>4</sub> nanosheet. After ion-exchange reaction, the core-shell hierarchical structures still maintained (Figure 10c-(d)).

# 4. Hierarchical Structure Based on 2D Nanomaterials for Rechargeable Lithium Batteries

It is well known that structure and morphology of the active materials, as well as its supporting matrixes, have significant influence on the electrochemical performance of the electrode. Currently, rational design and synthesis and assembly of the hierarchical structure based on 2D nanomaterials have aroused considerable research interest owing to their unique properties over the layered 2D nanomaterials, such as large surface areas, high porosity and shortened pathways for charge/mass transport, which make them promising candidates for high-performance electrode for RLBs. **Table 1** gives the summary of the electrochemical performance of various hierarchical structured electrode materials for RLBs.

## 4.1. Non-Aqueous Lithium-Ion Battery

Non-aqueous LIBs are extensively investigated as essential energy storage devices due to their high operating voltage, large specific energy, long cycling life, relatively light weight, enhanced safety and low toxicity. The common 2D nanomaterials, such as TMOs, TMDs and Graphene and its derivatives, have been deeply explored as functional materials for LIBs in recent years. Different active materials show quite different energy densities and power densities due to their chemical structures and physical properties. Graphene as an anode materials for LIBs possesses larger specific capacity owing to its the huge specific surface area and numerous edge sites for hosting lithium. Moreover, the diffusion distance of lithium ion (Li<sup>+</sup>) in few-layered graphene was short, leading to improved rate performance. However, the outstanding electrochemical performance of few-layered graphene suffered from aggregation and re-stacking of individual graphene nanosheets. This issue could be addressed by the recently developed 3D graphene aerogels (GAs), which was assembled by cross-linked individual graphene sheets and exhibiting a continuously interconnected macroporous network, large surface area, low mass density, and high electrical conductivity.<sup>[190,191]</sup> Zhong and co-workers reported a hierarchical porous GAs as an anode for LIBs.<sup>[42]</sup> The interconnected macro-porosity was obtained by uniformly loading Co<sub>3</sub>O<sub>4</sub> nanoparticles (20 and 50 nm) during the hydrothermal process, and the mesoporous were produced by the decomposition of the carbon source via an in situ carbothermal reactions (Figure 11a). Owing to the hierarchical macropores GAs framework, and abundant mesopores on graphene sheets for Li<sup>+</sup> diffusion and adsorption, the hierarchical porous GAs exhibited superior electrochemical performance including a high reversible specific capacity of 1100 mA h g<sup>-1</sup> at a current density of 0.1 A g<sup>-1</sup>, outstanding cycling stability and excellent rate performance (Figure 11b-d). Although considerable progress has been made to develop porous graphene anodes for LIBs, they usually exhibited a relative low volumetric capacity due to their low packing density (<0.5 g cm<sup>-3</sup>). To counter this, Qu's group prepared a nitrogen-doped holey-graphene monoliths (NHGMs) with both hierarchical porous microstructure and high density of 1.1 g cm<sup>-3</sup> (Figure 11e-f).<sup>[43]</sup> The SEM image shown in Figure 11g presents a compact microstructure of NHGMs, which could deliver a high volumetric capacity. The STEM image presents the holey structures in the individual graphene sheets (Figure 11h), which could promote ion diffusion and access to the graphene surface regardless of the compact stacking structure. Moreover, the doped N atoms could also enhance electrochemical reactivity and electronic conductivity. Thus, the NHGMs as an anode for LIBs demonstrated





**Figure 10.** a) Schematic illustration of the two-step synthesis of metal oxide ( $Co_3O_4/NiO$  and ZnO/NiO) core/shell nanowire arrays directly on various substrates. b) SEM image of the  $Co_3O_4/NiO$  core/shell nanowire arrays. Inset: TEM characterization of  $Co_3O_4/NiO$  core/shell nanowire arrays. Reproduced with permission.<sup>[176]</sup> Copyright 2012, American Chemistry Society. c) Schematic illustration and corresponding SEM images of the fabrication of CoS core nanowires@NiCo\_2S\_4 shell NSAs: a) Ni foam substrate, b) CoO nanowire arrays, c) CoO core nanowires@NiCo\_2O\_4 shell NASs, d) CoS core nanowires@NiCo\_2S\_4 shell NSAs. Inset in (b), (c), and (d): enlarged image of CoO nanowire arrays, CoO core nanowires@NiCo\_2O\_4 shell NSAs and CoS core nanowires@NiCo\_2S\_4 shell NSAs. Reproduced with permission.<sup>[172]</sup> Copyright 2015, Royal Society of Chemistry.

a high volumetric capacity (up to 1052 mA h cm<sup>-3</sup>) and excellent cycling stability (over 1200 cycles) at high mass loading of  $2.75 \text{ mg cm}^{-2}$  (Figure 11i,j).

Besides being used as anode materials for LIBs, hierarchical structured graphene and its derivatives can also serve as the supporting backbone for the hosted active materials, which can directly serve as conductive current collectors in the fabrication process of electrode. Hierarchical structured graphenebased materials, including GFs, GAs and GSs, present the disordered conductivity network, high specific surface area, highly flexible and large void space, which appear as a promising 3D supporting matrix for electrochemically active materials in LIBs applications. Much research has been based on these disordered graphene network structures as backbones for LIBs and has reported on the exploration of novel functionalities by deposition of active materials on various hierarchical structured graphene and its derivatives, such as Fe<sub>3</sub>O<sub>4</sub>@G/ GFs,<sup>[36]</sup> SnO<sub>2</sub>/GFs,<sup>[37]</sup> MoS<sub>2</sub>/GFs,<sup>[38]</sup> G@NiSb/Sb@NFs,<sup>[114]</sup> Si/GSs,<sup>[63,64]</sup> Fe<sub>2</sub>O<sub>3</sub>/GAs,<sup>[44,45]</sup> Fe<sub>2</sub>O<sub>3</sub> nanocubes/N-GAs,<sup>[46]</sup> Fe<sub>3</sub>O<sub>4</sub>/N–GAs,<sup>[47]</sup> Fe<sub>3</sub>O<sub>4</sub>/GAs,<sup>[48]</sup> Fe<sub>3</sub>O<sub>4</sub> nanospheres/GAs,<sup>[49]</sup> SnO<sub>2</sub>/N-GAs,<sup>[50]</sup> CoCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>/GAs,<sup>[51]</sup> CoO/GAs,<sup>[52]</sup>  $MnO_2/GAs^{[53]}$   $MnO_2/N$ - $GAs,^{[54]}$   $TiO_2/GAs,^{[55,56]}$  Spinel-type oxides/ $GAs,^{[57]}$   $MoS_2$  and  $FeOx/GAs,^{[58]}$   $MoS_2/Gas,^{[59,60]}$  As a typical example, Gao et al. fabricated  $Fe_2O_3/GAs$  via a novel solvothermal-induced self-assembly process, using  $Fe(OH)_3$  sol as precursor.<sup>[44]</sup> The hybrid electrode manifested a superior rate capability (930, 660 and 520 mA h g<sup>-1</sup> at 500, 2000 and 4000 mA g<sup>-1</sup>, respectively) and excellent prolonged cycling stability at high rates (733 mA h g<sup>-1</sup> during 1000 charge/discharge cycles at 2000 mA g<sup>-1</sup>), demonstrating its great potential for application in high performance LIBs. Its superior electrochemical performance can be ascribed to the synergistic interaction between uniformly dispersed  $Fe_2O_3$  particles with high capacity and then conductive 3D graphene network with a large surface area and an interconnected porous structure.

 $MoS_2$  as anode materials for rechargeable LIBs can deliver a higher capacity (670 mA h g<sup>-1</sup> with 4e<sup>-</sup> transfer reaction per formula) than the commercial graphite material (372 mA h g<sup>-1</sup>). However, the inferior rate performance of  $MoS_2$  anode ascribed to their poor electronic conductivity is still the main challenge. Shen et al. reported a honeycomb-like  $MoS_2$  nanoarchitectures@GFs structure by introducing ultrathin  $MoS_2$  nanosheets

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 Table 1. The main hierarchical structure constructed by using 2D nanomaterials and their applications in RLBs.

2D materials	Hier	archical Structure	Application	Electrochemical Properties	Ref. [42]
Graphene	3D porous network structure	GAs	LIBs (Anode)	1100 mA h g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	
		NHGMs	LIBs (Anode)	1052 mA h cm <sup>-1</sup> after 1200 cycles	[43]
		Fe <sub>2</sub> O <sub>3</sub> NPs/GAs	LIBs (Supporting Matrixes)	733 mA h cm $^{-1}$ after 1000 cycles at 2000 mA g $^{-1}$	[44]
		Fe <sub>2</sub> O <sub>3</sub> NPs/GAs	LIBs (Supporting Matrixes)	995 mA h cm $^{-1}$ after 50 cycles at 100 mA g $^{-1}$	[45]
		Fe <sub>2</sub> O <sub>3</sub> nanocubes/N-GAs	LIBs (Supporting Matrixes)	1121 mA h cm $^{-1}$ after 500 cycles at 500 mA g $^{-1}$	[46]
		Fe <sub>3</sub> O <sub>4</sub> NPs/N-GAs	LIBs (Supporting Matrixes)	1130 mA h cm $^{-1}$ after 200 cycles at 100 mA g $^{-1}$	[47]
		Fe <sub>3</sub> O <sub>4</sub> NPs/GAs	LIBs (Supporting Matrixes)	730 mA h g $^{-1}$ at 1600 mA g $^{-1}$	[48]
		Fe <sub>3</sub> O <sub>4</sub> nanospheres/GAs	LIBs (Supporting Matrixes)	1059 mA h cm $^{-1}$ after 150 cycles at 93 mA g $^{-1}$	[49]
		SnO <sub>2</sub> NPs/N-GAs	LIBs (Supporting Matrixes)	905 mA h cm $^{-1}$ after 1000 cycles at 2000 mA g $^{-1}$	[50]
		CoCO <sub>3</sub> and Co <sub>3</sub> O <sub>4</sub> NPs/GAs	LIBs (Supporting Matrixes)	1102/1012 mA h g $^{-1}$ after 80 cycles at 100 mA g $^{-1}$	[51]
		CoO NPs/GAs	LIBs (Supporting Matrixes)	503 mA h cm $^{-1}$ after 50 cycles at 4800 mA g $^{-1}$	[52]
		MnO <sub>2</sub> NPs/N-GAs	LIBs (Supporting Matrixes)	909 mA h cm $^{-1}$ after 200 cycles at 400 mA g $^{-1}$	[54]
		TiO <sub>2</sub> nanocrystals/GAs	LIBs (Supporting Matrixes)	99 mA h g $^{-1}$ at 5000 mA g $^{-1}$	[55]
		TiO <sub>2</sub> NPs/GAs	LIBs (Supporting Matrixes)	165 mA h g <sup>-1</sup> after 200 cycles at 1 C	[56]
		Spinel-type oxides NPs/GAs	LIBs (Supporting Matrixes)	330 mA h cm $^{-1}$ after 1000 cycles at 4.5 A g $^{-1}$	[57]
		G@NiSb/Sb@NF	LIBs (Supporting Matrixes)	90% retention after 200 cycles at 500 mA $g^{-1}$	[114]
		3D GSs-Si	LIBs (Supporting Matrixes)	2050 mA h g $^{-1}$ over 200 cycles at 200 mA g $^{-1}$	[64]
		S-PDMS-GF	Li-S (Supporting Matrixes)	$\approx$ 0.07% capacity decay per cycle over 1000 cycles	[39]
		3D GF-rGO/S	Li-S (Supporting Matrixes)	63.8% retention after 350 cycles	[40]
		N, S doped GAs/S	Li-S (Supporting Matrixes)	~0.078% capacity decay per cycle up to 500 cycles	[181]
		Li <sub>2</sub> S /B, N doped GAs	Li-S (Supporting Matrixes)	403/397 mA h $g^{-1}$ after 300 cycles at 0.5 C	[182]
		PGFs/S	Li-S (Supporting Matrixes)	852 mA h g $^{-1}$ after 500 cycles; 609 mA h g $^{-1}$ at 5 C	[67]
		Graphene foam/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	Round-trip efficiency of 80% with a stable discharge voltage at 2.8 V	[68]
		rGO aerogels/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	$\approx 20000 \text{ mA h } g_c^{-1}$ at 1 A $g_c^{-1}$	[61]
		3D bicontinuous porous N,S doped G cathode/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	10400 mA h $g^{-1}$ at 200 mA $g^{-1}$	[70]
		N-GAs/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	5978 mA h g <sup>-1</sup> at 3.2 A g <sup>-1</sup>	[62]
		$3D$ porous $G + Ru/O_2$	Li-O <sub>2</sub> (Cathode)	17710 mA h g <sup>-1</sup> at 200 mA g <sup>-1</sup>	[69]
		3D nanoporous N-doped G+RuO <sub>2</sub> /O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	2000 mA h g $^{-1}$ over 100 cycles at 400 mA g $^{-1}$	[66]
		GSs+Co/CoO/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	4292 mA h g $^{-1}$ at 200 mA g $^{-1}$	[65]
		Co <sub>3</sub> O <sub>4</sub> /GF/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	583 mA h g $^{-1}$ after 62 cycles at 50 mA cm $^{-2}$	[183]
	Hollow structure	Graphene nanocapsules	LIBs (Anode)	1373 mA h g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	[84]
		HGS-S	Li-S (Supporting Matrixes)	419 mA h g <sup>-1</sup> after 1000 cycles at 1 C	[85]
		N-doped G/G tubes/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	5300 mA h $g_{cat}^{-1}$ at 50 mA $g_{cat}^{-1}$	[86]
	Self-supported nanoarrays	VAGAs	LIBs (Anode)	380 mA h g <sup>-1</sup> at C/3	[87]
		SiNPs@GNS on VAGAs	LIBs (Supporting Matrixes)	$88\%$ retention after 50 cycles at 150 mA $g^{-1}$	[88]
		CeOx on VAGAs	LIBs (Supporting Matrixes)	1008 mA h g <sup>-1</sup> after 100 cycles at C/3	[89]
		SnO <sub>2</sub> NPs on VAGAs	LIBs (Supporting Matrixes)	210 mA h $g^{-1}$ after 5000 cycles at 9 A $g^{-1}$	[90]
		Sn@G on VAGAs	LIBs (Supporting Matrixes)	400 mA h g $^{-1}$ after 5000 cycles at 6 C	[91]
		S-G nanowall	Li-S (Supporting Matrixes)	400 mA h g <sup>-1</sup> after 170 cycles at 4 C	[92]
TMOs	3D porous net- work structure	FeOx (85%)/G aerogels	LIBs (Anode)	270 mA h g <sup>-1</sup> after 1500 cycles at 80 C	[58]
		MnO2 (60%)/G aerogels/O2	Li-O <sub>2</sub> (Cathode)	314 mA h $\sigma^{-1}$ after 40 cycles at 50 mA $\sigma^{-1}$	[53]

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## Table 1. Continued.

2D materials	Hierarchical Structure		Application	Electrochemical Properties	Ref.
		g-C <sub>3</sub> N <sub>4</sub> /G aerogel/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	17300 mA h g $^{-1}$ <sub>(composite)</sub> at 0.2 mA cm $^{-1}$	[184]
		3D-G-MnO <sub>2</sub> /O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	1350 W h Kg <sup>-1</sup> after 110 cycles at 0.333 mA cm <sup>-1</sup>	[41]
		MnO <sub>2</sub> aerogels/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	4581 mA h g <sup>-1</sup> at 50 mA g <sup>-1</sup>	[185]
		NiCo <sub>2</sub> O <sub>4</sub> aerogels/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	10137 mA h $g^{-1}$ at 200 mA $g^{-1}$	[186]
	Hollow structure	Fe <sub>3</sub> O <sub>4</sub> hollow sphere	LIBs (Anode)	457 mA h g <sup>-1</sup> at 10 A g <sup>-1</sup>	[71]
		TiO <sub>2</sub> (B) tubular	LIBs (Anode)	160 mA h g <sup>-1</sup> after 400 cycles at 5 C	[72]
		Co-Mn-HTS	LIBs (Anode)	478 mA h g $^{-1}$ at 2000 mA g $^{-1}$	[81]
		Yolk-shell TiO <sub>2</sub> microsphere	LIBs (Anode)	113 mA h g <sup>-1</sup> after 100 cycles at 10 C	[75]
		CoMn <sub>2</sub> O <sub>4</sub> hollow sphere	LIBs (Anode)	894 mA h g $^{-1}$ after 65 cycles at 100 mA g $^{-1}$	[79]
		Graphene-encapsulated ZnNiCoO <sub>x</sub> microsphere	LIBs (Anode)	420 mA h g <sup>-1</sup> after 900 cycles at 1 C	[80]
		Core-shelled NiCo <sub>2</sub> O <sub>4</sub> hollow sphere/O <sub>2</sub>	Li-O <sub>2</sub> (Cathode)	8658 mA h g $^{-1}$ at 100 mA g $^{-1}$	[82]
		Porous Co <sub>3</sub> O <sub>4</sub> microsphere/O <sub>2</sub>	A-Li-O <sub>2</sub> (Cathode)	1250 mA h g $^{-1}$ over 110 h at 0.05 mA cm $^{-1}$	[187]
	Self-supported nanoarrays	$\alpha\text{-}Fe_2O_3$ nanosheets on Ti foil	LIBs (Anode)	908 mA h g $^{-1}$ after 60 cycles at 100 mA g $^{-1}$	[93]
		Bi <sub>2</sub> O <sub>3</sub> nanosheets on Ti foil	ALIBs (Anode)	78 W h $kg^{-1}$ at a power density of 170 W $kg^{-1}$	[188]
		$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanosheets on Cu foil	LIBs (Anode)	877 mA h g $^{-1}$ after 1000 cycles at 2 C	[189]
		CuO nanoarrays on Cu foil	LIBs (Anode)	651 mA h g $^{-1}$ after 100 cycles at 0.5 C	[98]
		Mesoporous NiO nanosheets on CC	LIBs (Anode)	758 mA h g $^{-1}$ after 150 cycles at 700 mA g $^{-1}$	[165]
		CoO nanosheets on NF	LIBs (Anode)	1000 mA h g $^{-1}$ after 100 cycles at 1 A g $^{-1}$	[94]
		MnCo <sub>2</sub> O <sub>4</sub> nanosheets on CC	LIBs (Anode)	2 mA h cm <sup>-2</sup> at 1600 mA cm <sup>-2</sup>	[105]
		NiCo <sub>2</sub> O <sub>4</sub> nanowire arrays on NF	LIBs (Anode)	976 mA h g <sup>-1</sup> at 200 mA g <sup>-1</sup>	[106]
		Co₃O₄@MnO₂ nanoneedles array on NF	LIBs (Anode)	387 mA h g <sup>-1</sup> at 960 mA g <sup>-1</sup>	[111]
		Tubular CuO/CoO on Cu foam	LIBs (Anode)	466 mA h g $^{-1}$ after 2000 cycles at 2 A g $^{-1}$	[110]
		Fe <sub>2</sub> O <sub>3</sub> @NiO core-shell arrays	LIBs (Anode)	1047 mA h g $^{-1}$ after 50 cycles at 200 mA g $^{-1}$	[107]
		CuO@Co <sub>3</sub> O <sub>4</sub> core-shell arrays	LIBs (Anode)	810 mA h g $^{-1}$ after 500 cycles at 1000 mA g $^{-1}$	[108]
		TiO <sub>2</sub> @SnO <sub>2</sub> core-shell arrays	LIBs (Anode)	530 mA h g $^{-1}$ after 30 cycles at 1600 mA g $^{-1}$	[109]
		Co <sub>3</sub> O <sub>4</sub> @NiO/C core-shell arrays	LIBs (Anode)	1053 mA h g <sup>-1</sup> after 50 cycles at 0.5 C	[112]
ſMDs	3D porous network structure	MoS <sub>2</sub> (85%) /G aerogels	LIBs (Anode)	no capacity decay after 3000 cycles at 140 C	[58]
		MoS <sub>2</sub> (80%) /G aerogels	LIBs (Anode)	1200 mA h g <sup>-1</sup> at 100 mA g <sup>-1</sup>	[59]
		MoS <sub>2</sub> (84%)/G aerogels	LIBs (Anode)	1216 mA h g $^{-1}$ after 30 cycles at 76 mA g $^{-1}$	[60]
		Honeycomb-like MoS <sub>2</sub>	LIBs (Anode)	800 mA h g $^{-1}$ at 5000 mA g $^{-1}$	[38]
	Hollow structure	MoS <sub>2</sub> tubular structure	LIBs (Anode)	500 mA h g $^{-1}$ at 5000 mA g $^{-1}$	[73]
		MoS <sub>2</sub> microbox	LIBs (Anode)	700 mA h g <sup>-1</sup> at 1000 mA g <sup>-1</sup>	[74]
	Self-supported nanoarrays	$MoS_2$ nanosheets s on ACF	LIBs (Anode)	418 mA h g $^{-1}$ after 200 cycles at 0.5 A g $^{-1}$	[34]
		${\sf MoS}_2$ nanosheets on G	LIBs (Anode)	620 mA h g $^{-1}$ after 1000 cycles at 4 A g $^{-1}$	[160]
		$MoS_2$ nanosheets on CC	LIBs (Anode)	3.5 mA h cm <sup>-2</sup> at 0.15 mA cm <sup>-2</sup>	[169]
		ReS <sub>2</sub> nanowalls on GF	LIBs (Anode)	539 mA h g <sup>-1</sup> at 1000 mA g <sup>-1</sup>	[101]

into the 3D GFs structures.<sup>[38]</sup> Owning to their high surface area, massive defect sites, highly conductive substrates directly as current collector, and 3D interpenetrating structure, Li<sup>+</sup> storage capability of honeycomb-like MoS<sub>2</sub> nanoarchitectures@GFs can

be greatly improved (Figure 12a). As shown in Figure 12b,c, honeycomb-like  $MoS_2$  nanoarchitectures@GFs possessed excellent electrochemical properties, including high initial coulombic efficiency, high specific capacity, high rate performance





**Figure 11.** a) Schematic diagram of the morphological formation of hierarchical porous GA. b) Snapshot, SEM image and TEM image of the asprepared hierarchical porous GA-50 (50 refers to 50 nm  $Co_3O_4$  NPs used in the preparation process), indicating macroporous structures of GAs and mesoporous structures of individual graphene sheets. c) Discharge/charge voltage curves for the first three cycles of hierarchical porous GA anode at 0.1 A g<sup>-1</sup> with a voltage window of 0.1–3.0 V. d) Rate capability of the hierarchical porous GA-50 anode. Reproduced with permission.<sup>[42]</sup> Copyright 2015, Nature Publishing Group. e–f) Snapshots of NHGM in a water-filled bottle, the bubble at the surface of NHGM implies its porous structure. g) SEM image of the compressed NHGM and h) the STEM image show the holy structure in the individual graphene sheets. i) Rate capacities of NHGM at different current densities. j) The discharge capacity retention and Coulombic efficiency of NHGM. Reproduced with permission.<sup>[43]</sup> Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

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**Figure 12.** a) Schematic illustration of the additional active edge sites at the intersection of adjacent  $MoS_2$  nanosheets and the fast transportation of electron in honeycomb-like  $MoS_2@GFs$ . b) Cycling behaviors of the honeycomb-like  $-MoS_2@GFs$ , hollow sphere- $MoS_2@GFs$  and hollow sphere- $MoS_2$  electrodes at a current density of 200 mA h g<sup>-1</sup>. c) Cycling behavior of the honeycomb-like  $MoS_2@GFs$ , hollow sphere- $MoS_2@GFs$  and hollow sphere- $MoS_2$  electrodes at various current densities. d) Nyquist plots of the honeycomb-like  $MoS_2@GFs$ , hollow sphere- $MoS_2@GFs$  and hollow sphere- $MoS_2$  electrodes at various current densities. d) Nyquist plots of the honeycomb-like  $MoS_2@GFs$ , hollow sphere- $MoS_2@GFs$  and hollow sphere- $MoS_2$  electrodes obtained by applying a sine wave with amplitude of 5 mV over the frequency range from 200 KHz to 0.01 Hz; the smallest circle diameter indicated the lowest of resistance in honeycomb-like  $MoS_2@GFs$  electrode (magnified figure at the high frequency and the equivalent circuit model of the studied system, inset). Reproduced with permission.<sup>[38]</sup> Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. e–f) Schematic illustration of the lithiation processes for alloy anodes based on different electrode configuration: (e) bare particles undergone large volume variation and tended to pulverize upon repeated cycling, leading to possible exfoliation of active component from current collector and rapid capacity decay, (f) The graphene-protected active particles grown on 3D Ni foam not only provided a self-adaptive and stretch graphene protection layer for buffering volume changes caused by repeated cycling, but also effectively inhibited the exfoliation of active component upon cycling. g) The discharge and charge profiles of G@NiSb/Sb@NFs at different current densities. h) The cycling performance of G@NiSb/Sb@NFs between 0.2 and 1.4 V at 500 mA g<sup>-1</sup> except the initial seven cycles cycled at 0.01–2.0 V. Reproduced with permission.<sup>[114]</sup> Copyright 2015, Wiley-VC

and stable cycleability, much better than those of hollow MoS<sub>2</sub> sphere@GFs and hollow sphere-MoS<sub>2</sub>. To investigate the kinetic differences of these MoS<sub>2</sub> electrodes, electrochemical impedance spectroscopy (EIS) was performed (Figure 12d). It can be seen that the diameter of the semicircle for honey-comb-like MoS<sub>2</sub> nanoarchitectures@GFs in the high-medium frequency region was the smallest one compared with those of hollow sphere-MoS<sub>2</sub> @GFs and hollow sphere-MoS<sub>2</sub>, which indicated that honeycomb-like MoS<sub>2</sub> nanoarchitectures@GFs possessed the lowest contact and charge-transfer resistances. This result clearly validates that the 3D graphene-backboned honeycomb-like MoS<sub>2</sub> architecture can not only ensure a high conductivity of the overall electrode, but also largely enhance the electrochemical activity of MoS<sub>2</sub> anode materials during the cycle processes.

Alloy anode materials, such as silicon (Si), antimony (Sb) and Tin (Sn), have triggered tremendous potential application in next-generation rechargeable LIBs owing to their safe operation potential and high theoretical capacities of 660–4200 mA h g<sup>-1</sup> (4200 mA h g<sup>-1</sup> for Si, 660 mA h g<sup>-1</sup> for Sb, and 990 mA h g<sup>-1</sup> for Sn).<sup>[192–194]</sup> Such high capacities are due to the accommodation of more Li atoms per active atom (e.g., Li<sub>4.4</sub>Si, Li<sub>3</sub>Sb, and Li<sub>4.4</sub>Sn). However, such alloy anodes still suffer from severe problems of poor electrical conductivity, large volume change upon lithiation/delithiation, and exfoliation of active materials from current collector, eventually resulting in loss of electrical contact, rapid capacity decay, and poor cycling performance

(Figure 12e).<sup>[193]</sup> Considering these drawbacks, 3D porous graphene structure is the optimal supporting matrix for alloy anodes, which not only shows a good elasticity as well as high electric conductivity and good mechanical robustness during Li<sup>+</sup> insertion/extraction, but also maintains a good physical contact with active particles upon cycling, realizing the sustainable contact and protection of the active materials (Figure 12f). Yu et al. fabricated a graphene-protected 3D Sb-based anodes on NF (G@NiSb/Sb@NFs) by a facile electrostatic-assembling and subsequent confinement replacement strategy.<sup>[114]</sup> When tested as a anode for LIBs, such binder/conductive addictivefree electrode exhibited reversible capacities of 442 mA h g<sup>-1</sup> at 100 mA  $g^{-1}$  and 295 mA h  $g^{-1}$  at 1000 mA  $g^{-1}\text{,}$  and capacity retention of above 90% after 200 cycles at 500 mA g<sup>-1</sup> (Figure 12g,h). GS, as a novel 3D graphene network scaffold, has been developed due to its low-cost and elastic properties, which have enormous potential for large-scale application in flexible electrodes. Yang and his co-workers developed a 3D graphene-silicon (G-Si) networks by employing commercially available sponge as template and GO nanosheets as the building block.<sup>[64]</sup> The resulting 3D G-Si networks with porous structure, good flexibility, ultrathin hybrid walls, and high electrical conductivity can not only minimize the volume change of Si during the cycling processes but also provide numerous open channels for the easy access of electrolyte and well maintain the high electrical conductivity of overall electrode, thus facilitating the rapid diffusion of both Li<sup>+</sup> and e<sup>-</sup>. Compared to

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**Figure 13.** a) The FESEM and b) TEM image of the hierarchical  $Fe_3O_4$  hollow spheres. c) Cycling performance at a current density of 500 mA g<sup>-1</sup>. d) Rate performance at various current densities from 0.5 to 10 A g<sup>-1</sup>. Reproduced with permission.<sup>[71]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. e) The FESEM and f) TEM image of the TiO<sub>2</sub> (B) HTs after annealing at 350 °C for 2 h. g) Cycling performance of the TiO<sub>2</sub>(B) HTs and TiO<sub>2</sub>(B) NSs at different current rates. h) Long-term cycling performance of the TiO<sub>2</sub>(B) HTs and TiO<sub>2</sub>(B) NSs at a constant current rate of 5 C and coulombic efficiency of the TiO<sub>2</sub>(B) HTs during the cycling process. Reproduced with permission.<sup>[72]</sup> Copyright 2015, Royal Society of Chemistry.

the Si/Graphene mixture, the 3D G–Si network has significant improved performance as an anode material for LIBs in terms of reversible capacity, cycling stability and high-rate capability.

Additionally, VAGAs were also employed to circumvent the limitation for these high-capacity anode materials. The oriented graphene nanoarrays as a novel active substance carriers exhibit several advantages for energy storage devices compared with disordered graphene network structures. First, each ultrathin VAGAs are vertically connected to the conductive collector such that the both sides of nanosheets introduce more reaction sites for active materials. Second, the VAGAs display 3D continuous conductive network, allowing for efficient electron transfer and reduced ion-transport pathways. Thirdly, the interspace between the oriented nanosheets can sufficiently accommodate the volume change of anchored active materials during the cycling process. Most importantly, due to the use of this directly grown structure, the need for binders or conducting additives that add additional weight is eliminated. Wang and co-workers have reported SiNPs@GNS-VAGAs electrodes by in situ growth strategy, which exhibited a high reversible capacity value of 1528 mA h  $g^{-1}$  at 150 mA  $g^{-1},$  relatively good cycle stability (88.6% after 50 cycles) and fast charge/discharge rate (412 mA h g<sup>-1</sup> at 8 A g<sup>-1</sup>).<sup>[88]</sup>

TMOs have received ever-growing research interest as potential anode materials for next-generation LIBs in view of their high theoretical capacities, low costs, environmental benignities, as well as natural abundances. However, the TMOs usually suffer from poor cyclabilities and rate capabilities caused by the huge volume/structural variation during operation and slow electrochemical kinetics. Hollow nanostructure as an available architecture for electrochemical advice applications can effectively alleviate the volume variation, offer an express transport path for electrons (e<sup>-</sup>) and ions and maximize the active interfacial sites, thereby providing unusual advantages over their traditional bulk materials as ideal electrode structures. Lou and co-workers synthesized a highly uniform hierarchical Fe<sub>3</sub>O<sub>4</sub> hollow spheres composed of ultrathin porous nanosheets as anode material to enhance their electrochemical performance for LIBs (Figure 13a,b).<sup>[71]</sup> The as-prepared hierarchical Fe<sub>3</sub>O<sub>4</sub> hollow spheres exhibited stable cycling performance over 100 discharge-charge cycles at a current density of 500 mA g<sup>-1</sup> (Figure 13c). Even at a high current density of 10 A  $g^{-1}$ , these hierarchical Fe<sub>3</sub>O<sub>4</sub> hollow spheres can deliver a stable capacity of about 457 mA h g<sup>-1</sup> (Figure 13d). Such remarkable high-rate performance of these Fe<sub>3</sub>O<sub>4</sub> hollow spheres was significantly superior to that of most nanostructured Fe<sub>3</sub>O<sub>4</sub> materials, and was even better than that of  $Fe_3O_4/C$  nanocomposites. This hierarchical architecture based on nanosheet sub-units of active materials and the hollow structure offered a robust and porous framework, large electrode/electrolyte contact area, and reduced Li<sup>+</sup> diffusion distance, all of which benefited the electrochemical reaction kinetics in the electrode. On the other hand, such architecture improved capability to accommodate huge volume variation during cycling. Compared with simple single-shelled spherical structures, one-dimensional (1D) tubular-like structures ensure better electron transport. Moreover, tubular nanostructures typically offer higher surface area, resulting in more active interfacial sites. Lou's group fabricated a TiO<sub>2</sub>(B) HTSs constructed from randomly oriented TiO<sub>2</sub>(B) nanosheets (Figure 13e,f).<sup>[72]</sup> When evaluated as an anode for LIBs, the tubular structured TiO<sub>2</sub>(B) showed excellent electrochemical lithium storage properties with a high capacity, excellent rate capability and cycling stability, which was superior to that of TiO<sub>2</sub>(B) nanospheres (NSs) (Figure 13g,h).

Hollow nanostructured polynary TMOs have improved their electrochemical performance compared to corresponding hollow nanostructured mono-TMOs due to their enhanced electrochemical activity and electrical conductivity, thus becoming next-generation anode candidates for LIBs. Lou et al. synthesized a serious of M-Mn oxides HTSs (M = Co, Ni, Cu, and Zn) composed of binary TMOs nanosheets.<sup>[81]</sup> As a typical example, the as-synthesized Co-Mn-HTS materials were evaluated as anode materials for LIBs and exhibited a high specific capacities of 1193, 980, 796, 639, and 478 mA h g<sup>-1</sup> at the current ENERGY MATERIALS \_\_\_\_\_ www.advenergymat.de

> С 0.2 C 0.5 C 1020 (ויגיו (V vs.  $200\,\mathrm{nm}$ 150 200 250 300 350 Capacity (mAhg') d Charge Li.Ti.O Discharge 400 250 200 200 200 100 50 50 100 150 200 250 300 400 450 500 550 600 650 700 Cycle number

**Figure 14.** a) SEM image of the hierarchical yolk-shell TiO<sub>2</sub> microspheres obtained at 400 °C. b) The enlarged SEM of individual TiO<sub>2</sub> microspheres and the inset in (b) is the low magnification SEM image of the corresponding yolk-shell sphere. c) Discharge-charge profiles and d) cycle and rate performances at various discharge-charge rates. e) The Li<sup>+</sup> insertion process of the hierarchical yolk-shell TiO<sub>2</sub> microspheres and the formation of  $Li_2Ti_2O_4$  nanocrystallites. Reproduced with permission.<sup>[75]</sup> Copyright 2015, Royal Society of Chemistry.

densities of 200, 400, 800, 1200, and 2000 mA g<sup>-1</sup>, respectively. Moreover, the obtained electrode showed good capacity retention from the second cycle onward and the discharge specific capacity can be maintained at 981 mA h g<sup>-1</sup> after discharging/ charging for 30 cycles.

Even though advanced hollow structure provides an effective way to generate high-performance electrode materials with great advantages over bulk and solid materials, the large interior cavities result in a low tap density and low volumetric energy density of the TMOs anode materials for LIBs. In this regard, fine tuning the shell thickness and void size of the hollow structures are required to take full advantage of the hollow structured electrode materials without compromising the volumetric energy density too much. Recently, yolk-shell nano-architectures with distinctive core@void@shell configuration have attracted considerable attention due to their high volumetric energy density, as well as offer the unique advantages of hollow structured TMOs nanomaterials, when used as the anode material for LIBs. The inner core of such yolk-shell structure improved the rate capability as well as the volumetric energy density of the electrodes by increasing the weight fraction of the electrochemically active component. The internal void space ensured easy and complete penetration of the electrolyte into the particles and accommodated the volume expansion during repeated charging/discharging processes. The thin shell reduced the diffusion pathway for Li<sup>+</sup> and e<sup>-</sup> transport, facilitating Li<sup>+</sup> insertion/ extraction. Su et al. prepared hierarchical yolk-shell TiO<sub>2</sub> microspheres constructed by 2D nanosheet-based porous (15 nm) shell and the nanocrystal-based inner mesoporous (3 nm) core (Figure 14a,b).<sup>[75]</sup> Compared to the traditional hollow structures,

the yolk-shell structure significantly improved structural stability, volumetric specific capacity and energy density, enabling the TiO<sub>2</sub> anode material with superior lithium storage performance. The obtained results show that yolk-shell TiO<sub>2</sub> microspheres demonstrated excellent Li<sup>+</sup> capacity with outstanding cycle performance and superior rate capability at different rates for >700 cycles, retaining a 225 mA h g<sup>-1</sup> reversible capacity after 100 cycles at 1 C. In particular, the reversible capacity can still be maintained at 113 mA h g<sup>-1</sup> after 100 cycles at 10 C (Figure 14c,d). As illustrated in Figure 14e, the improved Li<sup>+</sup> storage capability mainly attributed to their unique yolk-shell TiO<sub>2</sub> structure with outer 2D nanosheets constructed porous shell and inner nanoparticle-aggregated mesopore core structures. Moreover, the new formed Li<sub>2</sub>Ti<sub>2</sub>O<sub>4</sub> crystalline can deliver additional surface capacity, further enhancing the Li<sup>+</sup> storage capacity. In the future work, the fabrication of high-quality hierarchical yolk-shell structured 2D nanomaterials as electrode materials will be an attractive research direction in developing high-performance LIBs.

Recently, self-supported TMOs nanoarrays are of great interest in the fabrication of the advanced electrode for LIBs, which can also effectively solve the intractable problems of the common TMOs, such as poor  $\text{Li}^+/\text{e}^-$  transport kinetics and pronounced volume change during the  $\text{Li}^+$  insertion/extraction processes. Particularly, the fabrication of hierarchical nanoarray electrodes without the auxiliary binders and conductive additives not only can simplify electrode processing, but also can enhance charge transfer efficiency and improve gravimetric capacity. Fe<sub>2</sub>O<sub>3</sub> as a typical TMO, has been constructed into a hierarchical porous nanoarrays and demonstrated an

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REVIEW

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**Figure 15.** a) Typical SEM images of NiO nanosheets grown on CC with well-established textiles at low magnifications; Inset: the photographic images of CC before and after NiO nanosheets grown be perpendicularly over the entire carbon fiber. c) Magnified TEM image of the NiO nanosheets. Inset: magnified image of the selected part presented that the nanosheets were grown perpendicularly over the entire carbon fiber. c) Magnified TEM image of the NiO nanosheets. Inset: magnified image of the selected part presented that the nanosheets were grown perpendicularly over the entire carbon fiber. c) Magnified TEM image of the NiO nanosheets. Inset: magnified image of the selected part showing the mesoporous feature of the NiO nanosheets. d,e) Electrochemical characterizations of NiO nanosheets/CC based half-cells: d) The rate performance of the electrode at various current densities. e) Capacity of the electrode versus cycle numbers at the current density of 700 mA  $g^{-1}$  and the corresponding Coulombic efficiencies. f) Cycling performance of the bent full LIBs based on NiO electrodes cycled at 700 mA  $g^{-1}$  in the voltage range of 1.0–4.0 V for 100 cycles. g) Schematic of the mesoporous NiO nanosheets/CC based full LIB. h) Photograph of full mesoporous NiO nanosheets/CC based LIB under bending. i) Photograph of "HUST" pattern lightened by an as-assembled LIB under bending. Reproduced with permission.<sup>[165]</sup> Copyright 2014, Nature Publishing Group.

appearing structure for electrochemical energy storage.<sup>[93,189]</sup> For example, Lou et al. reported a general method to directly grow porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets on Ti foil as integrated electrodes for LIBs.<sup>[93]</sup> The resultant porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets arrays demonstrated excellent cycling performance with high capacity of 908 mA h g<sup>-1</sup> after 60 cycles at a current density of 100 mA g<sup>-1</sup>, and showed a good rate capability with a capacity of 573 mA h g<sup>-1</sup> at 2000 mA g<sup>-1</sup>. The hierarchical CuO nanoarrays,<sup>[98]</sup> which directly connected on conductive Cu foil, exhibited a high-rate capability of 561.6 mA h g<sup>-1</sup> at a 10 C rate and an excellent cycling stability of 651.6 mA h g<sup>-1</sup> after 100 cycles at a 0.5 C rate.

Compared with 2D conductive substrates, the 3D porous conductive substrates with enhanced growth sites of active materials, accessible pathways for the penetration of electrolyte and fast  $\text{Li}^+/\text{e}^-$  transport path is greatly beneficial for the improvement of the specific areal capacity, specific gravimetric

capacity and high-rate performance of the arrays electrode for LIBs. For instance, hierarchical mesoporous NiO nanosheets arrays were directly grown on 3D carbon cloth (CC) substrate, which can be directly used as a self-supported anode for LIBs.<sup>[165]</sup> As shown in Figure 15a, the woven structures of CC were well preserved and wrapped by numerous NiO nanosheets. From the enlarged view shown in Figure 15b, it can be observed that the nanosheets were grown perpendicularly over the entire carbon fiber. The as-prepared NiO nanosheets interconnected each other and exhibited porous nanostructure with abundant open space and electroactive surface (inset of Figure 15b). The TEM image in Figure 15c reveals that the NiO nanosheets were mesoporous with a pore size of 2-5 nm, which could be related to the rapid release of water molecules during the annealing process. The highly porous texture of NiO nanosheet and their interconnected open space provided high electrode/electrolyte contact area, which facilitated the diffusion

of Li<sup>+</sup> ions, meanwhile the direct contact of NiO nanosheets on CC as the current collector greatly promoted the e<sup>-</sup> transport. Moreover, the mass loading of NiO nanosheets (1.77 mg cm<sup>-2</sup>) was much higher than that of the NiO nanosheets grown on Ni substrate (0.167 mg cm<sup>-2</sup>),<sup>[195]</sup> indicating that a higher energy density can be achieved by the direct growth of nanostructures on 3D conductive substrate compared to that on 2D planar substrate. As a consequence, the electrode exhibited excellent cycling stability (758.1 mA h  $g^{-1}$  after 150 cycles at 700 mA  $g^{-1}$ ) and good rate capability (426 mA h  $g^{-1}$  at 2000 mA  $g^{-1}$ ), which was much higher than that of NiO nanosheet on Ni foil (Figure 15d,e). Considering the highly flexible characteristics of the CC substrate, Tang et al. fabricated flexible full LIBs using the mesoporous NiO nanosheets/CC as self-supported anodes. The schematic of the fabricated flexible full battery and the photograph of their soft packaged full battery under bending are shown in Figure 15g,h. The bent full battery can not only deliver a relatively high reversibility capacity of 500 mA h g<sup>-1</sup> after 100 cycles, but also supply power under greatly bending state (Figure 15f,i). As another example, Wang et al. fabricated an ultrathin and highly ordered CoO (NSAs) on a NF substrate.<sup>[94]</sup> The CoO nanosheets were porous and consisted of the homogeneous overlapped nanocrystals, which was beneficial to the mass transport of electrolyte and diffusion of Li<sup>+</sup> ion. When investigated as a self-supported anode in LIBs, the CoO NSAs showed improved cycling performance with a discharge capacity of 1000 mA h  $g^{-1}$  at 1 A  $g^{-1}$  after 100 cycles, and the rate capability was excellent with a capacity of 520 mA h g<sup>-1</sup> at 10 A g<sup>-1</sup>. For the spinel binary TMO nanoarrays, hierarchical MnCo<sub>2</sub>O<sub>4</sub> NSAs as a typical example were grown on CC through a simple hydrothermal method.<sup>[105]</sup> The as-prepared electrode exhibited a high areal capacity of 3.0 mA h cm<sup>-2</sup> at a current density of 800 mA cm<sup>-2</sup>, excellent cycling stability (Coulombic efficiency was almost 100% except for the first cycle) and good rate performances (2 mA h  $cm^{-2}$  at 1600 mA  $cm^{-2}$ ).

Hierarchical TMOs nanoarrays with higher complexity have stimulated tremendous research interest because their multicomponents and multi-level architecture could provide potential complementary and/or synergistic effect, such as higher electrochemical activity, much more efficient utilization of the remaining free space, more efficient electrolyte penetration and structural stability. Particularly, complex hierarchical nanoarrays electrode composed of 2D binary TMOs are highly anticipated to show remarkable electrochemical performance for advanced LIBs. For example, hierarchical porous nickel cobaltate (NiCo2O4) nanowire cluster arrays derived from NiCo2O4 NSAs on NF were fabricated via a hydrothermal method with a subsequent annealing process.<sup>[106]</sup> The NiCo<sub>2</sub>O<sub>4</sub> nanosheets were grown on the surface of the NF at the initial stage, and then acted as roots to grow the multi-directional NiCo2O4 nanowires. This unique structure significantly enhanced the electroactive surface areas of the NiCo2O4 arrays, leading to better interfacial/chemical distributions at the nanoscale, fast Li<sup>+</sup> and e<sup>-</sup> transfer and good strain accommodation during repeated cycling process. When tested as an anode for LIBs, it displayed a high reversible capacity of 976 mA h  $g^{-1}$  at a rate of 200 mA g<sup>-1</sup> with good cycling stability and rate capability.

Various TMOs usually suffer from diverse thorny problems related to their inherent characteristics, such as low theoretical

capacity for special TMOs with an intercalation mechanism, large volume expansion for special TMOs with a conversion or alloying mechanism. Hierarchical nanoarrays composed of two or multi-components TMOs has received considerable attention for offering a good solution to the problems associated with these single-phase TMOs. For instance, Cheng et al. reported highly ordered 3D Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> hierarchical porous nanoneedles array on NF by a stepwise hydrothermal process.<sup>[111]</sup> The porous Co<sub>3</sub>O<sub>4</sub> nanoneedles as core materials were electrically connected to the 3D porous NF, which can reduce the resistance for e- transport between the current collector and the electrode, leading to high-rate capability. Ultrathin sheetslike MnO2 increased the contact area with electrolyte, enabling a fast and sufficient redox reaction. On the other hand, the outer MnO<sub>2</sub> nanosheet can protect the inner structure of Co<sub>3</sub>O<sub>4</sub>, enhancing the cycle stability. As a result, excellent electrochemical performances such as high reversible capacity of 1060 mA h  $g^{-1}$  at a rate of 120 mA  $g^{-1}$  as well as cycling stability and rate capability (387.5 mA h  $g^{-1}$  at 960 mA  $g^{-1}$ ) were achieved, which were better than that of the individual component of Co<sub>3</sub>O<sub>4</sub> nanoneedles and MnO<sub>2</sub> nanosheets. Zhang et al. reported an in situ growth of 3D hierarchical tubular CuO core/CoO shell nanoarrays on Cu foam (Figure 16a,b).<sup>[110]</sup> When evaluated as a self-supported anode for LIBs, the 3D hierarchical tubular CuO core/CoO shell nanoarrays were shown to retain a capacity of 1364 mA h  $g^{-1}$  at 100 mA  $g^{-1}$ after 50 cycles (Figure 16c). A capacity of 342 mA h  $g^{-1}$  was maintained at a high rate of 4000 mA  $g^{-1}$  (Figure 16d). Even cycled at 2000 mA g<sup>-1</sup> for 2000 cycles, the cell can maintain a high capacity of 466 mA h g<sup>-1</sup>, which is superior to the theoretical capacity of graphite (372 mA h  $g^{-1}$ ) (Figure 16e). The superior electrochemical performance of the fabricated tubular CuO core/CoO shell array anodes can be attributed to the welldesigned hierarchical tubular structure and synergistic effects of the hollow CuO nanotube backbone combined with branched CoO nanosheet shells, endowing a good mechanical adhesion, fast charge transfer pathways, shortened Li<sup>+</sup> diffusion lengths and the enhanced strain accommodation (Figure 16f). As states above, the key of this composite nanoarray was to select suitable active materials as core and shell materials, which could exhibit a potential synergistic effect with remarkably enhanced electrochemical performances compared to the single TMOs.

Recently, more attentions have been drawn to a serious of TMDs as anode materials because of their significantly higher specific capacity than traditional insertion electrode materials. Among them, monolayer or few-layer MoS<sub>2</sub> nanosheets as a highly promising anode for LIBs were reported to facilitate fast Li+ intercalation/deintercalation process, resulting in an increase in the reversible capacity of MoS<sub>2</sub>. However, the monolayer or few-layer MoS2 nanosheets often suffer from poor cycling stability, which is attributed to the large volume change, and re-stacking of MoS2 nanosheets during the cycling.<sup>[196]</sup> An emerging and effective avenue is the rational design and synthesis of active materials with hierarchical hollow structures. Wang and co-workers constructed hierarchical tubular structures assembled from single-layered MoS<sub>2</sub> nanosheets as an anode for LIBs.<sup>[73]</sup> The as-prepared assembled MoS<sub>2</sub> tubes had a high specific surface area and mesopores resulting from the disordered assembly of ultrathin MoS<sub>2</sub> layers. Such a high





**Figure 16.** a) low-magnification and b) high-magnification SEM images of hierarchical tubular CuO core / CoO shell nanoarrays, inset in (b) indicates that the CoO nanosheets were fully coated onto the CuO nanotube core with a good uniformity. c–e) Electrochemical performance of as-fabricated tubular CuO core / CoO shell nanoarrays anode on Cu foam: c) cycling performance in the voltage range of 3.0 and 0.01 V at 100 mA  $g^{-1}$ , d) rate capability in the current range of 100–4000 mA  $g^{-1}$ , e) long-term cycle performance at 2.0 A  $g^{-1}$ . f) Schematic illustration of pathways for e<sup>-</sup> conduction and Li<sup>+</sup> diffusion during electrochemical reaction process in tubular CuO core/CoO shell nanoarrays on Cu foam. Reproduced with permission.<sup>[110]</sup> Copyright 2015, Elsevier.

specific area of tubular structures with mesoporous could be desirable for energy storage application, which may facilitate the transport of Li<sup>+</sup> or active materials. Consequently, 3D assembled MoS<sub>2</sub> nanotubes exhibited excellent electrochemical performance, compared with un-assembled MoS<sub>2</sub> nanosheets and commercial MoS<sub>2</sub> powders. Notwithstanding these advances, the rational design and facile synthesis of MoS<sub>2</sub>-based hollow architectures with highly exposed active edge sites, large specific surface area and high stability still require further exploration. Later on, Lou's group reported novel shape of hollow structures, hierarchical microboxes constructed by ultrathin MoS<sub>2</sub> nanosheets, which were highly active for electrochemical reactions.<sup>[74]</sup> When evaluated as an anode material for LIBs, a high discharge capacity of 900 mA h g<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup> can be retained after 50 cycles, which was 98% of the discharge capacity of the second cycle.

Self-supported MoS<sub>2</sub> array were also fabricated and adopted to overcome this problem.<sup>[34,160,169]</sup> For example, Chen et al. reported a three-dimensional (3D) hierarchical MoS<sub>2</sub> nanoflake array on the surface of an ACF cloth.<sup>[34]</sup> The MoS<sub>2</sub> nanosheets were interconnected each other and developed into highly porous structure on the ACF surface, which can provide a large electrode–electrolyte interfacial area. Moreover, the interconnected carbon fiber exhibited fast transport paths for e<sup>-</sup> and Li<sup>+</sup>. When investigated as a self-supported electrode, a discharge capacity as high as 971 mA h g<sup>-1</sup> was attained at a current density of 0.1 A g<sup>-1</sup>, and the capacity fade was only 0.15% per cycle within 90 cycles. Even after 200 cycles at a high current density of 0.5 A g<sup>-1</sup>, the hierarchical MoS<sub>2</sub>/ACF cloth composite still showed a capacity of 418 mA h g<sup>-1</sup>.

Very recently,  $\text{ReS}_2$  is discovered to have extremely weak van der Waals interlayer coupling of  $\approx 18$  meV per unit cell

(for comparison, 460 meV for  $MoS_2$  per 2 × 2 conventional cell) and relatively large interlayer spacing of 6.14 Å (for comparison, 3.35Å for graphite and 6.15 Å for MoS<sub>2</sub>), which provides new opportunity for massive Li<sup>+</sup> to efficiently diffuse without significant volume expansion (Figure 17a). However, 2D layered materials, including ReS<sub>2</sub>, are always randomly oriented in a conventional stacked geometry, which can hinder Li+ diffusions and lower the complete utilization of the electrochemical surface area of the 2D layered materials. Fu et al. successfully realized the fabrication of ultra-uniformly distributed ReS<sub>2</sub> nanowalls vertically grown on 3D GF (V-ReS<sub>2</sub>/3D GF) through a CVD method.<sup>[101]</sup> For comparison, the layered ReS<sub>2</sub>, which was parallel to the 3D GF surface (L-ReS<sub>2</sub>/3D GF), is shown in Figure 17b. The SEM at the same magnification shown in Figure 17c displays that the ReS<sub>2</sub> nanowalls were vertically grown on NF and interconnected to produce random pore structure. As illustrated in Figure 17d, V-ReS<sub>2</sub> vertically standing on graphene exposed its sulfur edge sites, offering a full utilization of the sulfur edge and facile accommodation of any strain caused by Li<sup>+</sup> intercalation and deintercalation. However, the basal plane of L-ReS<sub>2</sub> hindered Li<sup>+</sup> from diffusing efficiently as they had a high-diffusion barrier height with fewer exposed active sites. When tested as the anode for LIBs, the L-ReS<sub>2</sub>/3D GF showed an initial discharge capacity of 539 mA g<sup>-1</sup>, but its capacity decreased rapidly in subsequent cycles. In contrast, the V-ReS<sub>2</sub>/3D GF electrode exhibited a high degree of stability (Figure 17e). To date, there are quite a few reports on the hierarchical TMDs nanoarrays as an exciting new anode for LIBs, which can be attributed to the fact that the TMDs show higher electrical conductivity, mechanical and thermal stability than those of their corresponding TMOs.



**Figure 17.** a) Schematic illustration of the weak interlayer interaction of  $\text{ReS}_2$ , compared with  $\text{MoS}_2$  and graphite. b–e) Comparison of horizontal growth  $\text{ReS}_2$  and vertical growth  $\text{ReS}_2$  and simulate reaction mechanism: b) SEM image of the  $\text{ReS}_2$  film reduced by sulfur; c) SEM image of the  $\text{ReS}_2$  nanowalls reduced by  $\text{H}_2$ S. d) Schematic illustration of lithium intercalation mechanism on edge sites and basal plane of  $\text{ReS}_2$ . e) The cycling performance of V-  $\text{ReS}_2/3D$  GF and  $\text{ReS}_2/3D$  GF anodes at a current density of 1000 mA g<sup>-1</sup>. Reproduced with permission.<sup>[101]</sup> Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

## 4.2. Non-Aqueous Lithium-Sulfur Battery

Non-aqueous Li-S batteries are being considered as the nextgeneration high energy storage system due to their high theoretical energy density (2567 W h kg<sup>-1</sup>).<sup>[197]</sup> Sulfur is also abundant, non-toxic, and inexpensive. Despite the great promise of Li-S batteries, many challenges need to be addressed before they can find the practical use. The low electrical conductivities of S, the intermediate polysulfide products, and the final Li2S product affect the utilization of the active S particles and the rate capability of the battery.<sup>[198]</sup> A large volume change (80%) between S and Li2S during charge/discharge due to the different densities of S (2.03 g cm<sup>-3</sup>) and Li<sub>2</sub>S (1.66 g cm<sup>-3</sup>) induces stress in the electrode and destroys its structural stability, which leads to rapid capacity decay.<sup>[199]</sup> Moreover, highly soluble polysulfides in the electrolyte, which can shuttle between the anode and cathode and form a deposit of solid Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S on the cathode and anode ("shuttle effect"), cause an irreversible loss of S, which leads to low coulombic efficiency, low cyclic capacity, and an increase in impedance.<sup>[200]</sup>

The adoption of hierarchical structured graphene and its derivatives nanomaterials as supporting matrix for Li-S batteries can partly overcome these obstacles, owing to their good conductivity, fast e<sup>-</sup>/Li<sup>+</sup> transport kinetics, large specific surface area, highly flexible characteristics. Cheng et al. prepared Sulfur-poly(dimethylsiloxane)/Graphene foam (S-PDMS/GF)

electrode for a flexible Li-S battery by using GF as a 3D conducting backbone and host for S particles.<sup>[39]</sup> The thin layer of PDMS was coated on the surface of the GF, which enabled the interconnected 3D network sufficiently robust, guaranteeing the flexibility of the electrode. As shown in Figure 18a, the S-PDMS/GF electrode with high sulfur loading of 10.1 mg cm<sup>-2</sup> still remained flexible. From the SEM observations, the sulfur particles filled the macropores of the interconnected GF network (Figure 18b). The electrode structure was also reconstructed and visualized by X-ray microtomography (XRM), as shown in Figure 18c,d, which confirmed that S and PDMS were distributed uniformly in the porous graphene network. The interconnected GF provided efficient e<sup>-</sup> pathways, offered vast void space to accommodate a significant amount of active substances, and held sufficient electrolyte (Figure 18e). With such a design, the S-PDMS/GF integrated electrode with a sulfur loading of 10.1 mg cm<sup>-2</sup> could deliver a high areal capacity of 13.4 mA h cm<sup>-2</sup> values that were much higher than those electrodes with S coated on Al foil (Figure 18f). Moreover, the S-PDMS/GF electrode also retained a stable cyclic performance with ≈0.07% capacity decay per cycle over 1000 cycles (Figure 18g). Ren et al. proposed a 3D GF-rGO hybrid nested hierarchical network macrostructure for Li-S batteries.<sup>[40]</sup> In this case, the GF framework with micrometer-scale pore size was tightly wrapped by rGO sheets connected to the macroporous GO aerogels. The highly conductive GF network can facilitate





**Figure 18.** a) Photographs of a flexible S-PDMS/GF electrode (7.5 cm  $\times$  7.5 cm) with 10.1 mg cm<sup>-2</sup> sulfur loading. b) SEM images of S-PDMS/GF electrodes with a high sulfur loading amounts of 10.1 mg cm<sup>-2</sup>. c) XRM 2D projections of S-PDMS/GF electrodes with 10.1 mg cm<sup>-2</sup> sulfur loading. d) 3D images of the reconstructed S-PDMS/GF electrodes with 10.1 mg cm<sup>-2</sup> sulfur loading (graphene and carbon black marked in gray, sulfur particles marked in yellow and PDMS marked in white. Reproduced with permission.<sup>[39]</sup> Copyright 2014, Elsevier. h) Cycling performance of the commercial Li<sub>2</sub>S rGO hybrid, Li<sub>2</sub>S /rGO, Li<sub>2</sub>S /B-doped graphene, and Li<sub>2</sub>S /N-doped graphene electrodes at various rates. i) XPS spectra of the surface chemical composition of GO, rGO, B-, and N-doped graphene aerogels. j) XPS spectra of B1s in B-doped graphene aerogel. k) XPS spectra of N1s in N-doped graphene aerogel. Reproduced with permission.<sup>[182]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

fast Li<sup>+</sup> and e<sup>-</sup> transport, and, more remarkable, the residual oxygen functional groups on the surface of rGO provided active sites to anchor the S particles and trap the soluble polysulfide intermediates within the electrode. The fabricated hierarchical porous structure not only enabled very high S loading but

also could serve as electrolyte reservoir and effectively accommodated the volumetric expansion of S nanoparticles. As a result, the GF–rGO/S cathodes exhibited a high areal capacity of 10.3 mA h cm<sup>-2</sup> at 0.2 C rate and a good cycling performance of 63.8% retention after 350 cycles at S loading of 9.8 mg cm<sup>-2</sup>.







**Figure 19.** a) Schematic diagram of vertically aligned S-G nanowalls as cathode for Li–S battery, facilitating the fast diffusions of both Li<sup>+</sup> and  $e^-$ . b) TEM image of the sectional slices of S-G nanowalls, revealing that sulfur nanoparticles were anchored in between of graphene layers and ordered graphene arrays in each S-G nanowalls. c–d) Electrochemical performance of vertically aligned S-G nanowalls as cathode material of Li–S battery: c) Selected discharge–charge profiles at various current rates from C/8 to 8C. d) Rate performance of S-G nanowalls cycled at various current rates and long cycle performance at a constant current rate of 4C. Reproduced with permission.<sup>[92]</sup> Copyright 2015, American Chemistry Society.

Meanwhile, heteroatom-doped (N, S, B) porous graphene frameworks have been heavily investigated and are widely used in energy storage systems.<sup>[201]</sup> The doped 3D porous graphene show improved electronic and chemical properties over pure 3D graphene originates in that the incorporation of doped ions can bring in more defect sites and free electrons for increased conductivity. For instance, N, S-codoped GAs as S carriers for Li-S battery exhibited fast reaction dynamics, reduced polarization and stabilized cycling performance with only 0.078% capacity decay per cycle up to 500 cycles.<sup>[181]</sup> The results of the first-principles calculations confirm that the heteroatoms-doped GAs additionally demonstrated strong chemical interaction between graphene and soluble lithium polysulfides. In their further work, they presented Li<sub>2</sub>S coated 3D N-, or B- doped GAs as cathode for high performance Li-S battery.<sup>[182]</sup> X-ray photoelectron spectroscopy (XPS) measurement revealed that the B1s (binding energy = 192.5 eV) and N1s (binding energy = 399.8 eV) signals emerged in the B-doped and N-doped GAs, respectively, implying a successful doping of B and N into the carbon backbone (Figure 18i). Moreover, the B1s and N1s XPS profiles of doped graphene aerogels in Figure 18j,k show the existence of many B/N-containing functional groups, which are formed predominately through substituting carbon atoms by heteroatoms on edges or defect sites in the basal plane of graphene, benefiting to the interaction between graphene and lithium polysulfides/Li<sub>2</sub>S. As a result, the Li<sub>2</sub>S/(B or N)-doped graphene electrodes exhibited significantly improved specific capacity, cycle stability, and rate capability along with a lowered voltage barrier relative to un-doped GAs cathodes, which mainly attributed to the 3D conductive framework with high electrical conductivity, strong adsorption abilities for polysulphides and rapid transport channels (Figure 18h). Other disordered 3D porous

graphene-based networks as supporting matrix were also extensively investigated in Li-S batteries. For instance, Zhang's group demonstrated a 3D graphene frameworks composed of abundant interconnected mesopores.<sup>[67]</sup> When the porous graphene frameworks (PGFs) applied as the conductive scaffolds for the S cathode in a Li-S cell, a very high initial discharge capacity of 1187 mA h g<sup>-1</sup> and S utilization of 71% were achieved at a current rate of 1.0 C. The capacity decreased to 852 mA h g<sup>-1</sup> after 500 cycles, which represented a fading rate of  $\approx 0.04\%$  per cycle since the second cycle. The rate performance also had a remarkably high capacity of 609 mA h g<sup>-1</sup> at 5.0 C.

The vertical graphene nanoarrays delivered cross-linked conductive networks with features of high density, large surface area and high porosity, resulting in the fast diffusions of both Li<sup>+</sup> and e<sup>-</sup>, the easy access of electrolyte and effective accommodation of the volume change of S during the cycling processes, which can also be considered as ideal S carriers. Yang et al. demonstrated a vertically aligned sulfur-graphene (S-G) nanowalls as a cathode for Li-S batteries (Figure 19a).<sup>[92]</sup> As shown in Figure 19b, S nanoparticles were homogeneously anchored in between of graphene layers and graphene arrays arrange in order and perpendicularly to the surface of substrates. The as-synthesized vertically aligned S-G nanowalls could be directly tested as an binder/conductive addictive-free S cathode for Li-S batteries, exhibiting a high reversible capacity of 1261 mA h  $g^{-1}$  at a current rate of C/8 and over 400 mA h  $g^{-1}$ after 170 cycles at a high current rate of 4 C with excellent cyclability (Figure 19d). Even at a current rate of 8 C, a high capacity of over 400 mA h g<sup>-1</sup> was obtained (Figure 19c).

Another effective hierarchical architecture for high performance Li-S battery is to infiltrate S into the hollow structured graphene as cathodes. The hollow interior endows extra free



space for alleviating the structural strain and accommodating the large volume variation during charge/ discharge process of S cathodes, giving rise to improved cycling stability. The large surface area entraps soluble lithium polysulfide for preventing the shuttle effect, leading to a higher reversible capacities and coulombic efficient. The permeable thin shell provided significantly reduced paths for both Li<sup>+</sup> ions and e<sup>-</sup> diffusion, resulting in a better rate capability. Zhang and co-workers prepared a hollow graphene spheres (HGSs) with a diameter of 10–30 nm, an specific surface area as high as 979 m<sup>2</sup> g<sup>-1</sup>, and a large pore volume of 1.98 cm<sup>3</sup> g<sup>-1</sup> as host to accommodate S for high-rate Li-S batteries.<sup>[85]</sup> The obtained HGSs-S cathode delivered high discharge capacities of 1520, 1058, and 737 mA h  $g^{-1}$ , which were obtained at different current densities of 0.1, 2.0, and 5.0 C, respectively. A high initial discharge capacity of 1098 mA h g<sup>-1</sup> and a discharge capacity of 419 mA h g<sup>-1</sup> were obtained after 1000 cycles at a current density of 1.0 C.

#### 4.3. Non-Aqueous Lithium-Oxygen Battery

Rechargeable non-aqueous Li-O2 batteries have recently attracted a great deal of attention due to their high theoretical specific energy (3500 W h kg<sup>-1</sup>), which is almost an order of magnitude higher than current LIBs (380 W h kg<sup>-1</sup>).<sup>[197]</sup> However, the Li-O<sub>2</sub> batteries are facing several fundamental challenges for practical applications, which are low reversible capacities, poor cycle life and inferior power density (rate capability). An important measure to improve rechargeability is to enhance reaction kinetics for the formation and decomposition of Li<sub>2</sub>O<sub>2</sub> by designing a nanostructured air electrode. Because the discharge product, Li2O2, continuously accumulates on the pores of an air electrode, it can potentially clog this electrode and become electrically disconnected, preventing further reactions. These isolated discharge products undergo minimal recharging. Therefore, the ideal O2 electrode should contain micrometer-sized open porosity, preventing pore clogging and promoting the diffusion of O<sub>2</sub> and Li<sup>+</sup>, and a degree of elasticity to release the strain produced during the charge and discharge processes. Moreover, the binder/conductive addictive-free O<sub>2</sub> electrode needs to be designed because tedious preparation process and multiple components of conventional O2 electrodes further complicate the electrochemistry and impose difficulties on the chemical analysis of Li-O<sub>2</sub> batteries. Recently, much efforts have been made to study the 3D porous network structured graphene<sup>[61,62,68-70]</sup> and TMOs<sup>[185,186]</sup> as O<sub>2</sub> electrode. For instance, Yan et al. developed graphene foams as O2 electrode by an electrochemical leavening (ECL) process of graphite paper in aqueous solution of Na<sub>2</sub>SO<sub>4</sub>.<sup>[68]</sup> The as-prepared graphene foam electrode annealed at 800 °C with a lower amount of structural defects ( $I_D/I_G = 0.07$  Figure 20a) delivered a round-trip efficiency of up to 80% with a stable discharge voltage at 2.8 V and a stable charge voltage below 3.8 V for 20 cycles (Figure 20b,c). Grey et al. demonstrated a highly efficient, rechargeable Li-O2 battery with extremely large capacities by using macroporous rGO aerogels as electrode and the redox mediator LiI, in a DME-based electrolyte.<sup>[61]</sup> The rGO framework can not only provide efficient diffusion pathways for all redox active species in the electrolyte and hence, a reduced

cell polarization and flatter electrochemical profile, but also permits the growth of discharge products of tens of micrometers in size, resulting in a capacity that is much closer to the theoretical value of  $\text{Li-O}_2$  batteries.

Furthermore, 3D porous graphene derivatives were also widely used as O<sub>2</sub> electrode for Li-O<sub>2</sub> electrode, which showed superior ORR/OER reactivity. Chen and co-workers developed novel 3D bicontinuous porous N- and S-doped graphene cathodes with a high accessible surface area, large porosity, and high conductivity for rechargeable Li-O<sub>2</sub> batteries (Figure 20d).<sup>[70]</sup> The heteroatom doping was effective to facilitate ORR and OER resulting from the modulated carbon electronic structure for enhancing oxygen adsorption and accelerating the reaction rate. As displayed in Figure 20g, the large pores and the inner channels of tubular nanostructures were filled with Li<sub>2</sub>O<sub>2</sub> particles after discharging, indicating a highly efficient oxygen and electrolyte delivery. After recharging, the Li2O2 particles completely disappeared, indicating a highly reversibility of Li<sub>2</sub>O<sub>2</sub> formation/decomposition in the nanoporous graphene cathodes (Figure 20h). Thus, 3D porous N-doped graphene cathode exhibited a high capacity of 10400 mA h g<sup>-1</sup>, and 3D S-doped graphene cathode presented a long lifetime up to 300 cycles at 1000 mA h g<sup>-1</sup> (Figure 20e,h). Qiu et al. further tailored the structure and properties of the skeletons within the N-GAs by introducing PS@PDA as template.<sup>[62]</sup> The FESEM and TEM images of N-GAs clearly shown in Figure 21a confirm that N-GA was composed of the interpenetrated and cross-linked graphene sheets in which abundant macro- and micro-sized interconnected nanocages within the 3D frameworks. The poresize distribution data shown in Figure 21b reveal that the abundant mesopores and macropores were presented in as-prepared N-GAs, which will be beneficial to the rapid transport of O2 and Li<sup>+</sup>, and the high specific area contributed to a large tri-phase (solid-liquid-gas) regions and a full exposure of active sites. It can be observed in Figure 21c that the N-GAs air electrode delivered higher ORR onset potential, lower OER onset potential, and higher ORR and OER peak currents compared with the GA and Super P air electrodes, suggesting a catalyst-like behavior of N-GA and a high catalytic activity for both ORR and OER processes. Benefiting from interconnected macro-porous and heteroatom-doped GAs, the Li-O2 batteries with NPGAs electrode exhibited a low overpotential, an excellent rate capacity of 5978 mA h  $g^{-1}$  at 3.2 A  $g^{-1}$ , and long cycle stability, especially at a large current density (54 cycles at 1 A g<sup>-1</sup>) (Figure 21d–f).

Although hierarchical structured graphene and its derivatives have been considered as ideal cathode material for Li–O<sub>2</sub> batteries, the inert nature of graphene gives rise to high charging overpotentials for Li<sub>2</sub>O<sub>2</sub> oxidation. To enhance the cathodic reaction kinetics for low charge overpotentials and high energy efficiency, it has been a prevalent approach to develop composite cathodes by loading catalysts, such as noble metal,<sup>[69]</sup> metal oxide<sup>[41,65,66,183]</sup> and others.<sup>[184]</sup> Among them, Ru-based catalysts have been found to be one of most effective catalysts to dramatically reduce the charge potentials of Li–O<sub>2</sub> batteries.<sup>[66,69]</sup> Chen et al. reported 3D nanoporous N-doped graphene with encapsulated RuO<sub>2</sub> nanoparticles as cathodes for rechargeable Li–O<sub>2</sub> batteries.<sup>[66]</sup> From the TEM image shown in **Figure 22**a, the graphene sheet was continuously interconnected as the skeleton of the porous structure to form bicontinuous nanoporous



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**Figure 20.** a) Raman spectra of graphene foams after annealing at 400, 600 and 800 °C in Ar. b–c) Electrochemical performance of the graphene foams as  $O_2$  electrodes for Li– $O_2$  batteries: a) Representative voltage profiles of the graphene foams at 100 mA g<sup>-1</sup>. c) Cycling performance of the graphene foam annealed at 800 °C at 100 mA g<sup>-1</sup>. Reproduced with permission.<sup>[68]</sup> Copyright 2013, Royal Society of Chemistry. d) Schematic representation of the nanoporous graphene based Li- $O_2$  battery. The high-porosity electrode with abundant graphene surfaces and interconnected open pore channels was structurally optimal for Li- $O_2$  reactions. e) Galvanostatic discharge–charge profiles of Li- $O_2$  cells using the nanoporous graphene cathodes. The cells were tested between 2.30 and 4.60 V at the current density of 200 mA g<sup>-1</sup>. f–g) Cross-sectional SEM images of f) fully discharged, and g) fully recharged N-doped graphene electrodes, showing the morphological evolution of the electrode during one full cycle. Inset in (f) illustrates that a Li<sub>2</sub> $O_2$  particle was also formed in the inner channel of tubular graphene. h) Cycling stability of the nanoporous N- and S-doped graphene based Li- $O_2$  cells using for all the tests. Reproduced with permission.<sup>[70]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

structures. The HRTEM image and chemical mapping confirm that the RuO<sub>2</sub> nanoparticles were homogeneously dispersed on graphene nanosheets (Figure 22b,c). As shown in Figure 22d, the N-doped graphene with encapsulated RuO<sub>2</sub> showed reduced overpotentials for both discharge and charge in comparison with the pure nanoporous N-doped graphene and graphene/RuO<sub>2</sub> hybrid electrodes, indicating that the uniformly dispersed RuO<sub>2</sub> nanoparticles can effectively enhance the formation and decomposition kinetics of Li<sub>2</sub>O<sub>2</sub>. Moreover, the as-prepared N-doped graphene with encapsulated RuO<sub>2</sub> electrode for Li–O<sub>2</sub> battery exhibited highly reversible cathodic reactions for over 100 discharge/charge cycles at the cutoff capacity of 2000 mA h g<sup>-1</sup> at 400 mA g<sup>-1</sup> (Figure 22e). The reversibility of Li<sub>2</sub>O<sub>2</sub> formation and decomposition on the nanoporous N-doped graphene encapsulated RuO<sub>2</sub> was further verified by ex-situ XRD of the fully discharged and recharged cathodes (Figure 22f). For the fully discharged electrode, broad diffraction peaks ( $2\theta = 35^{\circ}$ ) can be indexed as hexagonal Li<sub>2</sub>O<sub>2</sub>, while the characteristic Li<sub>2</sub>O<sub>2</sub> peaks completely disappeared after recharging.

Moreover, carbon-based cathode was unstable on charging above 3.5 V (in the presence of  $Li_2O_2$ ), oxdatively decomposing to form  $Li_2CO_3$  at carbon/ $Li_2O_2$  interfaces, which extremely hindered their large-scale application in  $Li-O_2$  batteries.<sup>[202]</sup> An efficient strategy to reduce the side reaction is to introduce high  $LiO_2$  adsorption energy materials into the graphene backbone. For example, Yan et al. prepared a 3D hierarchical Co/ CoO-Graphene-Carbonized Melamine Foam as  $O_2$  cathode

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**Figure 21.** a) FESEM image and TEM image (inset) of N-GA. b) Pore-size distributions of N-GA and GA. Inset: Nitrogen adsorption-desorption isotherms of N-GA and GA. c) The CV curves of the N-GA, GA, and Super P electrodes within a voltage widow of 2.0–4.5 V at a scanning rate of 0.1 mV s<sup>-1</sup>. d) Discharge-charge curves of N-GA, GA, and Super P electrodes with a fixed capacity of 1000 mA h g<sup>-1</sup> at a current density of 300 mA g<sup>-1</sup>. e) Discharge curves of N-GA electrode at different current densities. Inset: Schematic illustration of nanocage effects. f) Discharge capacity and roundtrip efficiency versus the cycle number for Li–O<sub>2</sub> cell with NPGA air electrode at 1 A g<sup>-1</sup>. Inset: Schematic illustration of N-doped graphene effect during charge. Reproduced with permission.<sup>[62]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure 22.** a) TEM image of nanoporous N-doped graphene with encapsulated  $RuO_2$  hybrid composite. b) TEM image of nanoporous N-doped graphene nanosheets with uniformly dispersed encapsulated  $RuO_2$  nanoparticles. c) EDX mappings of N, Ru and O elements and the overlapping maps of the three elements. d) The comparisons of discharge–charge profiles of Li– $O_2$  batteries based on three different cathodes at the capacity limits of 1000 mA h g<sup>-1</sup> at the current density of 200 mA g<sup>-1</sup>. e) The stable discharge–charge profiles of nanoporous N-doped graphene with encapsulated  $RuO_2$  electrodes for over 100 cycles collected at the capacity limits of 2000 mA h g<sup>-1</sup> at the current density of 400 mA g<sup>-1</sup>. f) Ex situ XRD patterns of pristine, fully discharged and fully recharged nanoporous N-doped graphene with encapsulated  $RuO_2$  electrodes. Reproduced with permission.<sup>[66]</sup> Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

for Li-O<sub>2</sub> batteries.<sup>[65]</sup> After incorporation of core-shell-like Co/CoO nanoparticles on 3D graphene sponge, the Li<sub>2</sub>O<sub>2</sub> was preferably grown on Co/CoO nanoparticles instead of graphene electrode surface due to the high LiO<sub>2</sub> adsorption of Co/CoO, reducing the side reaction at carbon/Li<sub>2</sub>O<sub>2</sub> interfaces. The obtained GS-Co/CoO hybrid electrode delivered a high capacity (7800 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>), remarkably improved cycle life (negligible capacity loss after 70 cycles at 100 mA g<sup>-1</sup> with a limited discharge depth of 500 mA h g<sup>-1</sup>) and outstanding rate capability (4292 mA h g<sup>-1</sup> at 200 mA g<sup>-1</sup>), exhibiting the great potential for the application in Li-O<sub>2</sub> batteries.

### 4.4. Aqueous Rechargeable Lithium Batteries

As presented above, we extensively reviewed the advances in the non-aqueous RLBs systems, which are garnering the major fraction of the current research on RLBs. However, safety and superfast charging performance are still two challenging issues to be solved for their application in large-scale energy storage systems. Aqueous RLBs (ARLBs) are of great potential to overcome aforementioned shortcomings, due to their uninflammability, high ionic conductivity and low-cost. So far, some reviews/papers were published with the scope on aqueous rechargeable lithium batteries.<sup>[203–208]</sup> However, the practical applications of aqueous RLBs are still limited by their poor cycling, unsatisfied rate capability and low energy density.

Recently, the cycling and rate capability of aqueous LIBs (ALIBs) have been greatly improved due to the exploration of new suitable electrode materials and advanced nanostructure, and they became a hot topic again.<sup>[209-214]</sup> For example, the porous Bi2O3 nanosheets arrays on Ti foil have been successfully prepared via a facile hydrothermal route and reported to show an excellent electrochemically store charges capability as a binder-free anode for ALIBs.<sup>[188]</sup> A remarkably high specific capacity (≈357 mA h g<sup>-1</sup> at 250 mA g<sup>-1</sup>), outstanding rate capability ( $\approx$ 41 mA h g<sup>-1</sup> at 7.5 A g<sup>-1</sup>) and good cycle life were demonstrated in a neutral mixed aqueous electrolyte (1.0 M LiCl and  $0.5 \text{ M Li}_2 \text{SO}_4$ ). Moreover, the Bi<sub>2</sub>O<sub>3</sub> nanoarray can be readily paired with the LiMn<sub>2</sub>O<sub>4</sub> cathode to construct a high-performance aqueous full battery. The energy density of LiMn<sub>2</sub>O<sub>4</sub>// Bi<sub>2</sub>O<sub>3</sub> (78 W h kg<sup>-1</sup> at a power density of 170 W kg<sup>-1</sup>) was far superior to their typical ALIBs (≈50 W h kg<sup>-1</sup>). Besides ALIBs, advanced hierarchitectures of eletrode materials were also utilized in aqueous Li-O2 (A-Li-O2) batteries.<sup>[187,215,216]</sup> As a typical example, Sun et al. have successfully synthesized a porous Co<sub>3</sub>O<sub>4</sub>/Cu microspheres for A-Li-O<sub>2</sub> batteries.<sup>[187]</sup> The obtained Co<sub>3</sub>O<sub>4</sub>/Cu microspheres exhibited mesoporous structure composed of the many nanoplate petals, which provided an efficient and stable bifunctional catalytic activity.

Doubtlessly, the introduction of hierarchy concept into the electrode materials could pave the pathway to more energetic ARLBs with energy densities competitive against the non-aqueous RLBs. However, only a few studies have been reported on ARLBs with hierarchitectures, especially constructed by 2D nanomaterials. The main reason restricting its development is the narrow potential window of the aqueous electrolyte (<1.5 V), and the water decomposition must be considered carefully in the choosing of electrode material for ARLBs. Very

recently, there have been a major breakthroughs that a new class of highly concentrated aqueous electrolytes ("Water-in-Salt" systems) was reported and successfully expanded the electrochemical stability window of aqueous electrolytes from 1.23 V to nearly 3.0 V, thus enabling many negative and positive electrodes materials applications that are otherwise impossible.<sup>[217–222]</sup> Undoubtably, the most obvious benefit of this optimized electrolyte system is an increased variety of available cathode/anode materials comparing with the traditional type of ARLBs. In the future work, various hierarchical structured electrolyte materials in this neotype aqueous electrolytes w\ould further push the energy densities of ARLBs closer to those of the state-of-the-art RLBs.

# 5. Conclusion

In this review, we have summarized the recent progress in 2D nanomaterials, with a focus on the rational construction of hierarchical structured electrode materials for rechargeable lithium batteries (RLBs). The hierarchical structures constructed by using 2D nanomaterials not only maintain their intrinsic attractive properties, but also offer additional features of hierarchical architecture, such as high porosity, quite larger specific surface area and improved electrical and mechanical properties. Thus, the obtained hierarchical structure nanomaterials can act as functional materials in advanced LIBs, Li-S and Li-O2 battery systems. Particularly, the 3D porous network structured graphene-based composite materials and TMOs/TMDs nanoarrays can serve directly as self-supported electrode, which could accelerate development of flexible and high-energy batteries. By exemplifying and analyzing in section 4, we highlight the importance of the structure engineering, providing more scientific insights into the smart design for future electrode in next-generation RLBs application.

Doubtless, the hierarchical architectural design of electrodes materials is an effective method to achieve high energy density, power density, cycling stability, and safety for RLBs. The current research on hierarchical structure based on 2D nanomaterials is still at embryonic stage, which has much room for development in the future work.

- 1. Although several construction methods of the hierarchical structures have been demonstrated, there is still need to make more efforts to explore more economic, green, convenient and scalable/large-scale production approach for the fabrication of advanced hierarchical structures.
- 2. For hierarchical nanoarrays as self-supported electrode for RLBs, the incorporated 3D conductive substrate largely increased the substrate mass and the void space of electrode, leading to low gravimetric capacity and specific volumetric capacity, respectively. Therefore, smart design of the conductive substrate for self-supported electrode is still a challenge to meet the requirement in industry.
- 3. Graphene-like 2D nanomaterials, such as black phosphorene, Mxenes, MOFs and 2D noble metal nanosheets, have been studied and shown great promise in applications electric, catalysis, energy storage, and more. However, current research on these novel 2D nanomaterials is still at



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planar configurations. One future research direction will be to assemble these novel 2D nanomaterials into hierarchical structures, and investigate their unique properties for energy storage application.

- 4. Till now, the chemical composition of 2D nanomaterials was based on single component, which only exhibited single properties. The atomic-scale heterostructure between the layered structures is an effective way to construct devices that integrates the properties of their isolated components. For instance, the Li adsorption and diffusion properties of the phosphorene/graphene (P/G) heterostructures have been fully explored by first-principles calculations.<sup>[223]</sup> The results suggest that the P/G can greatly improve the stiffness, conductivity, and the bonding strength of Li compared to the pristine single-layered phosphorus. Moreover, the P/G displayed the high lithium intercalation capacity without sacrificing the high mobility of Li in P/G. Based on these observations, the P/G is a very promising anode material for LIBs. In the future work, more atomic-scale heterostructured 2D nanomaterials are still waiting for systematic and deeper exploration by combining theoretical tools and experimental technology, which can accelerate the development of advanced hierarchical heterostructured electrode materials for RIBs.
- 5. The crystal orientation plays an important role in the superior electrochemical performance of the 2D nanomaterials.<sup>[19]</sup> For example, the previous research has found that LiFePO<sub>4</sub> nanoplates with the crystal orientation along the ac facet presented a much better rate-performance than that with the crystal orientation along the bc facet.<sup>[224]</sup> Therefore, the future hierarchitectured electrode materials based on 2D nanomaterials with preferred orientation could facilitate the fast and efficient transportation of Li<sup>+</sup>, and achieve high-power density.
- 6. Tough numerous studies have been conducted on the synthesis and application of hierarchical structure composed of 2D nanomaterials, state-of-the-art in situ and ex situ microscopic and spectroscopic techniques are still needed for a deeper understanding of the fundamental properties concerning the hierarchical structure nanomaterials, such as the studies of electrochemical reaction mechanisms, electrochemical dynamics of the electrode/electrolyte interfaces and bulk electrode materials, and structure properties of electrodes materials after long-term cycling, etc. Such studies will provide structure and functional mechanism of various structures, so as to give a guide to the design principle and synthesis of hierarchical structure composed of 2D nanomaterials with desired structural and functional characteristics for RLBs applications.
- According to the inspiration of "Water-in-Salt" system, further researches in combining hierarchical structured electrode materials (especially based on TMOs, TMDs and Graphenebased materials) and highly concentrated aqueous electrolyte system with low-cost lithium salts or interphase-forming additives, are necessary for more competitive energy densities (>200 W h kg<sup>-1</sup>) of ARLBs.

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