Carbon-based materials for advanced lithium metal batteries based on carbon units of different dimensions

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Abstract： We discuss recent advances in the control and design of carbon hosts/carriers based on their dimensionality (0D, 1D, 2D and 3D) for achieving high performance Li metal anodes. Representative modification strategies for these different carbons for studying their lithium affinity and their influence on the anode performance are highlighted and discussed. Prospects for the design of carbon hosts/carriers for practical rechargeable LMBs are discussed.

Key words: Carbon materials; Lithium metal anodes; Rate performance; Cyclic lifespan; Li dendrite growth

1 Introduction

Although lithium-ion batteries (LIBs) are undoubtedly the most important power source for consumers' portable electronic devices, the limited energy density of LIBs with traditional electrode materials (such as $LiCoO_2$ for cathode and graphite for anode) is insufficient to meet the ever-increasing requirements of a variety of emerging applications[1–3]. The development of high-performance cathode/anode materials has been an imperative and essential solution[4–8]. Li metal anodes possessing the ultrahigh theoretical specific capacity (3 860 mAh g^{-1}, which is about 10 times as high as traditional graphite anode) and low redox potential (−3.04 V *vs.* SHE), have been used as an applicatory anode material towards the next-generation high energy density rechargeable lithium batteries, such as Li-S, Li-Se, and Li-O_2 batteries[9–10]. Unfortunately, Li metal anodes are still subjected to uncontrollable dendrite growth, large volume expansion/shrinkage, and low repeated utilization, leading to poor cycling performance and unacceptable safety risks. These troubles have severely limited the access of lithium metal batteries (LMBs) to the market.

Progresses in addressing the above-mentioned obstacles include creating functionalized artificial solid electrolyte interphase (SEI) layers, modulating electrolyte components, optimizing electrolyte additives, constructing efficient Li metal hosts/carriers, and modifying separators[11–20]. Among them, using hierarchical frameworks as Li metal hosts/carriers is a promising solution to synergistically accommodate the large volume change and regulate the Li plating/stripping due to the efficient free space, high specific surface area, and effective electron/ion transport networks[21–28]. Carbon materials have been the ideal building units to construct hierarchical Li metal hosts/carriers, thanks to their good mechanical strength, high electronic mobility, stable electrochemistry, adjustable physicochemical properties, large specific surface area, light-weight, and low cost, etc[29–36]. The rigid carbon-based networks as Li metal hosts/carriers show threefold advantages: (1) High conductivity and large specific surface area are beneficial to reducing the local current density and effectively suppressing Li dendritic growth. (2) Excellent chemical and mechanical stability is conducive to maintain the structural/chemical integrity of the electrode in a highly reducing environment with high stress-strain. (3) Low density is good for maximizing

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the energy density of LMBs. However, normal carbon materials without additional sophisticated design have limited ability to regulate uniform Li deposition and alleviate large volume change due to their lithiophobic characteristics and limited internal space. A number of studies have been conducted to design carbonaceous hosts/carriers based on different design protocols, exhibiting enhanced performances in terms of competing rate capability, good cycling performance, and creditable Li metal utilization. Most of them focus on the creation and regulation of 3D hierarchical carbon skeleton, adjustment of wettability of carbon skeleton with metallic Li, and construction of effective electron/ion transport pathways[31–34].

In this review, we outline the latest representative progresses towards carbon host/carrier construction based on the variation of carbon unit dimensionality for achieving high performance Li metal anodes, and the strategies to adjust wettability of carbon hosts/carriers with metallic Li associated with different dimensionalities of carbon units. In the last section, prospects and directions on rational construction of advanced carbon hosts/carriers towards practical Li metal anodes with enhanced electrochemical performance for rechargeable LMBs are discussed.

2 0D carbon nanosphere-based hosts/carriers for Li metal anodes

0D carbon spheres, characterized by their excellent chemical stability, favorable electronic conductivity, and low cost, have found widespread application as conductive additives or ideal hosts/carriers for anchoring various electrochemically active cathode materials (e.g., S, Se, etc.) in lithium batteries, resulting in enhanced performance[37–42]. Recent efforts have focused on exploring the potential of well-designed carbon spheres to address the challenges faced by LMBs[43–48]. For example, Cui et al. introduced an amorphous hollow carbon nanosphere film that effectively regulated Li deposition and formed a stable artificial SEI when coated onto the surface of a Cu foil (Fig. 1)[43]. Compared with Cu collector, the low conductivity of carbon nanosphere coating facilitated Li deposition onto Cu surface, when an available and adjustable space for Li deposition benefited from free movement up and down of the carbon nanosphere coating during Li plating/stripping due to the weak bonding between carbon nanosphere coating and Cu collector. The well-engineered electrode exhibited a high Coulombic efficiency of approximately 99%. Although the hollow carbon nanosphere coating significantly mitigated Li plating/stripping and eliminated dendritic growth, the issue of pronounced thickness variation during Li plating/stripping beneath the carbon layer remains a formidable challenge.

The same research group investigated the nucleation phenomenon of metallic Li on different metal substrates and elucidated a substrate-dependent mechanism for Li nucleation/growth using binary phase diagrams. This finding provides guidance for the design of carbon hosts to regulate Li deposition. In light of this, they synthesized a carbonaceous nanocapsule with uniform dispersion of Au nanoseeds within hollow carbon spheres (Fig. 2)[44]. Compared to the hollow carbon spheres, the hybrid host exhibited a moderate Coulombic efficiency (98% over 300 cycles). The significant performance improvement was ascribed to the reduced Li nucleation barrier facilitated by the presence of Au nanoseeds within the hollow carbon spheres. Building on this principle, Song et al. developed a novel spherical carbon host modified with Ag nanoparticles, resembling a sesame ball structure (referred to as AgNPs@CS)[45]. The resulting AgNPs@CS electrode demonstrated outstanding cycling performance over 300 cycles, which can be attributed to its unique architecture. Specifically, the Ag nanoparticles promoted the lithiophilicity of carbon spheres, while the carbon spheres effectively prevented the agglomeration of lithiophilic Ag nanoparticles during charging and discharging processes.

Furthermore, the incorporation of heteroatom doping (such as S, N, F, O, etc.) has been observed as a potential approach to optimizing the affinity of carbonaceous hosts/carriers towards metallic Li[47–49]. For instance, Liu et al. developed a mesoporous carbon nanosphere with N/S co-doping (referred to as NS-

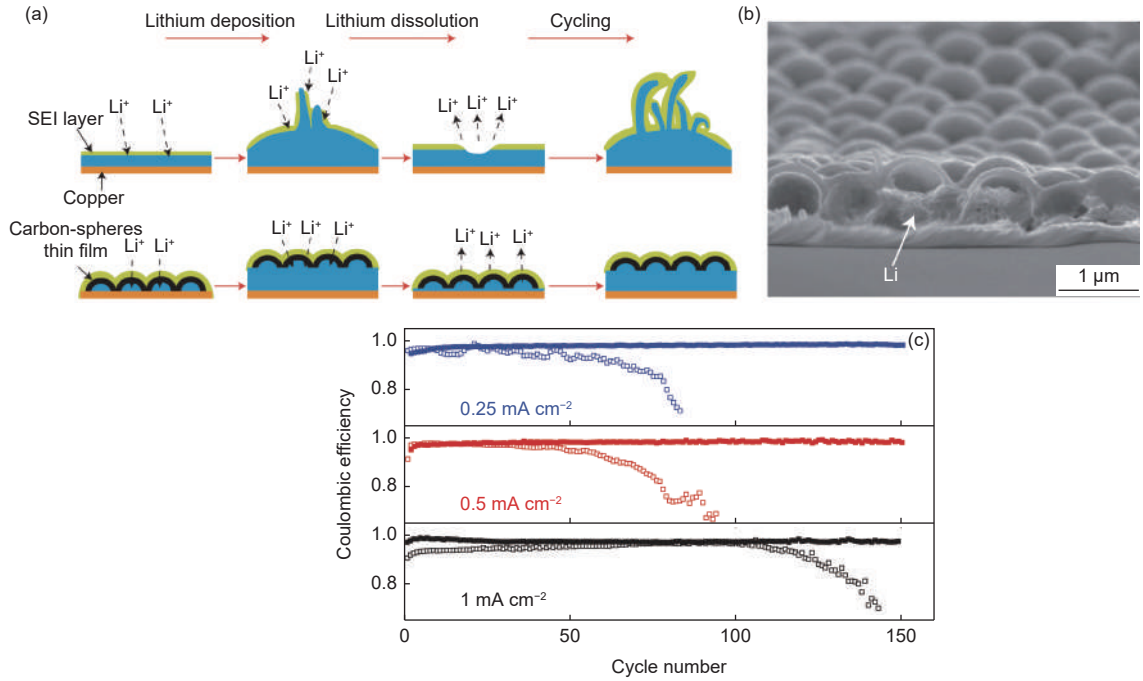

Fig. 1　(a) Schematic diagrams of the Li deposition/dissolution processes on different substrates. (b) SEM image after initial Li deposition. (c) Cycling performances at different current rates[43]. Reproduced by permission of Nature Publishing Group

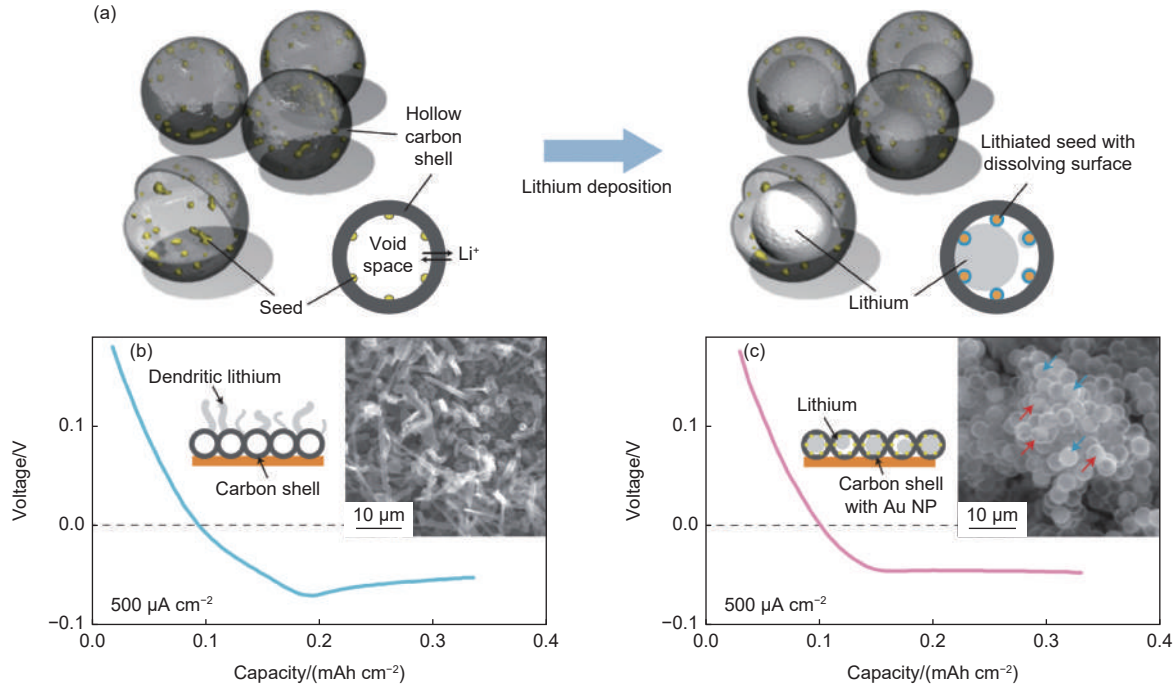

Fig. 2　(a) Schematic of the nanocapsules design. (b, c) Voltage profile of hollow carbon shells (b) without and (c)with Au NPs during Li deposition process, respectively[44]. Reproduced by permission of Nature Publishing Group

MC) as a multifunctional host for metallic Li using a two-step synthetic method involving in-situ polymerization followed by a facile pyrolysis process[48]. The resulting NSMC electrode exhibited a low Li nucleation overpotential (13 mV) and exceptional cyclic stability (2 700 h at 4 mAh cm^{-2}). When applied as the anode material in Li-$LiFePO_4$ batteries, the full cell demonstrated remarkable cyclic performance and high-rate capability. The observed performance enhancement can be attributed to several advantages. Firstly, the introduction of N and S dopants significantly improved the lithiophilicity of the carbon hosts,

thus reducing Li nucleation barrier and promoting dendrite-free Li deposition during plating/stripping processes. Secondly, the NSMC with homogeneous N/S co-doping facilitated the formation of a robust SEI layer, leading to enhanced interfacial stability. Thirdly, the ordered mesoporous channels within the NSMC structure facilitated rapid electron/ion transport, further enhancing its rate performance.

3 1D carbon nanotube/fiber-based hosts/carriers for lithium metal anodes

1D carbon materials, known for their lightweight nature, large specific surface area and excellent flexibility, have been identified as promising candidates for constructing 3D cross-linked conducting networks. These networks have been extensively investigated as a means to overcome the challenges associated with Li metal anodes[50–53]. In the following sections, we delve into the recent research advancements concerning the design of rational carbonaceous hosts/carriers based on carbon nanotubes (CNTs) and carbon fibers (CFs), respectively.

3.1 Carbon nanotubes

Carbon nanotubes (CNTs), with their unique and efficient 1D electron transport pathway, have been extensively utilized in the construction of lightweight and mechanically robust carbonaceous hosts/carriers for Li metal anodes[54–60]. For instance, Wang et al. developed a 3D self-supporting substrate using commercially available CNTs[54]. The resulting carbonaceous substrate exhibited a large specific surface area, which facilitated uniform current distribution and increased active sites, thereby promoting uniform Li deposition. Additionally, when the deposition voltage exceeded 0 V, the CNTs reacted with metallic Li, resulting in a “pre-lithiated” substrate that enhanced its affinity for metallic Li. As a result, the well-designed self-supporting electrode demonstrated high Coulombic efficiency and exceptional cycling performance. Ji et al. proposed and validated the use of a self-supporting expandable CNT paper as a stable host to adapt the significant volume expansion of the electrode[55]. Thanks to its unique structural design, the highly conductive CNT paper could effectively accommodate metallic Li without being destroyed, thereby achieving a satisfactory Coulombic efficiency (>97.5%), high area capacity (10 mAh cm^{-2}), and long cycle life (1 000 cycles).

Significant efforts have been dedicated to modifying CNT-based hosts/carriers by incorporating lithiophilic functionalities, such as N, O, ZnO, SiO_2, etc., to enhance uniform Li nucleation and growth[59–60]. Zhu et al. designed a hierarchical carbon scaffold known as CNTs-MC, where flexible CNTs grew on a relatively rigid graphitic scaffold through thermal annealing of melamine sponge[57]. The resulting CNTs-MC electrode exhibited impressive areal capacity (15 mAh cm^{-2} at 15 mA cm^{-2}) and favorable Coulombic efficiency (approximately 98% at 10 mA cm^{-2}). The improved performance can be attributed to several advantages. Firstly, the uniformly distributed CNTs with high conductivity effectively promoted homogeneous Li^+ distribution, enabling uniform Li deposition during the plating process. Secondly, the flexibility of CNTs allowed for the release of large stress/strain during charge/discharge cycles, contributing to a stable cycling performance. Thirdly, the co-doping of heteroatoms provided additional active sites, reducing the nucleation overpotential of metallic Li. Additionally, Guo et al. proposed and fabricated a rational microcage structure consisting of a CNT core and a porous silica insulative coating layer, known as H-SiO_2/CNTs, to serve as an efficient host for desirable Li deposition behavior and inhibition of Li dendrite growth[58]. In these well-designed microcages, the conductive CNTs facilitated efficient electron transport, while the insulative porous silica sheath regulated the Li^+ flux. This combination guided Li nucleation and growth behavior. Consequently, the hybrid electrode exhibited a high Coulombic efficiency of 99% (Fig. 3).

3.2 Carbon nanofibers

Carbon nanofibers (CFs), representing a typical example of 1D carbon materials, have been extensively studied to achieve enhanced performance in Li metal anodes due to their low cost, high specific sur-

face area, and excellent conductivity[61–65]. For instance, Guo et al. designed a 3D multifunctional carbon host utilizing graphitized carbon fibers (GCFs) for improved metallic Li storage[61]. The resulting GCFs electrode demonstrated low voltage hysteresis and good cyclic stability. It is believed that the outstanding conductivity and high specific surface area of the GCFs electrode significantly reduced the current density and effectively accommodated the volume change during charging/discharging processes.

In addition, incorporating lithiophilic substances (such as N, O, Si, ZnO, MgO, etc.) is a competitive strategy to enhance their wettability with metallic Li[66–68]. For instance, Zhang et al. designed a lithiophilic LiC_6 coating on the surface of CFs through a simple one-step rolling process to promote the wettability of CFs with metallic Li, attributed to the increased negativity of carbon atoms due to electron deviation[63]. With the lithiophilic LiC_6 interfacial layers, the resulting electrode exhibited a very low nucleation overpotential and demonstrated a long cycling life. When combined with a sulfur cathode, the pouch cell exhibited both high capacity retention (98% for 100 cycles) and high discharge capacity (3.25 mAh cm^{-2}). Hu et al. employed a novel rapid Joule heating technique to fabricate ultrafine Ag nanoparticles (AgNPs) anchored on the surface of CFs (Fig. 4)[64]. In this hybrid host design, the strong binding between AgNPs and the carbon matrix stabilized the electrode structure, and the AgNPs with zero overpotential regulated and guided Li nucleation and growth behavior. The electrode demonstrated a low voltage hysteresis of approximately 0.025 V and remarkable cycling performance over 500 h. Following a similar principle, Kang et al. presented an ultralight 3D carbon host with a bidirectionally lithiophilic gradient, achieved through a two-step magnetron sputtering method, denoted as CBG[65]. In the CBG structure, the Li-Zn alloy with high ionic conductivity facilitated Li-ion transportation throughout the entire electrode, transforming from top-down ZnO during the first cycle. Simultaneously, the bottom-up Sn with an applicable nucleation barrier induced preferential growth of metallic Li. Thanks to this well-designed structure, the CBG electrode exhibited low overpotential (8.4 mV), good cyclic stability (over 250 cycles), and moderate capacity (1 mAh cm^{-2}).

Indeed, electrospinning has been widely explored as an efficient method for designing hierarchical CFs and constructing effective metallic Li hosts/carriers[67, 69–72]. A notable example is the work by Kim et al., who presented a novel electrode structure comprising porous carbon nanofibers (PCNFs) fabricated through electrospinning and investigated the influence of their surface characteristics on Li plating/stripping behavior[69]. In the PCNFs electrode, the presence of open pores and oxygen doping on the surface played a crucial role in regulating Li depos-

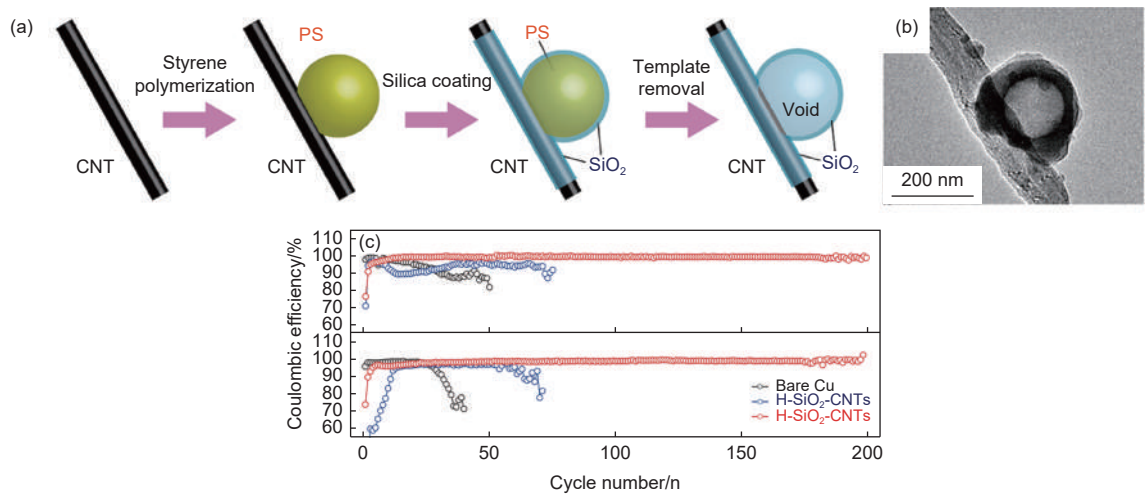

Fig. 3　(a) Synthetic approach. (b) TEM image, and (c) Coulombic efficiencies of the H-SiO_2/CNTs at different current densities (0.2 and 0.5 mA cm^{-2}, respectively)[58]. Reproduced by permission of American Chemical Society

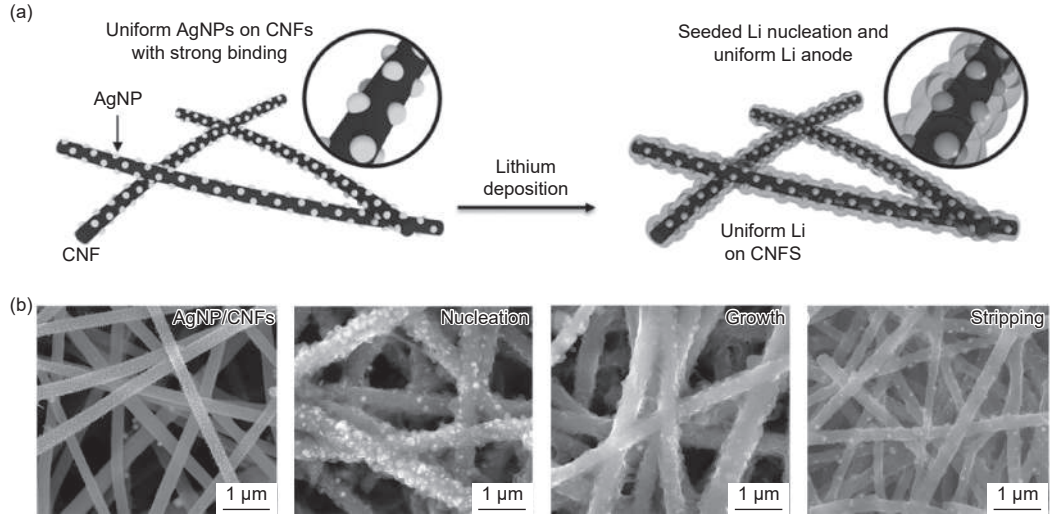

Fig. 4 (a) Schematic presentation of the uniform Li metal deposition process on 3D host modified by Ag nanoseeds, (b) SEM images of AgNP/CNFs at different cycle stages[64]. Reproduced by permission of Wiley-VCH

ition behavior and effectively inhibiting dendrite growth. These advantageous features of the PCNFs electrode resulted in enhanced cycling stability. When combined with a sulfur cathode, the full cell achieved an impressive energy density of 385 Wh kg^{-1}.

4 2D graphene-based hosts/carriers for lithium metal anodes

Graphene, a two-dimensional carbon nanosheet composed of one-atom-thick sp^2-bonded carbon atoms, has received significant attention as a promising candidate for addressing the challenges associated with Li metal anodes[73–85]. In the following discussion, we delve into the latest advancements in designing hierarchical graphene-based hosts/carriers based on various design principles for capturing/intaking metallic Li[86–103].

As an illustrative example, Cui et al. developed a unique composite electrode called reduced graphene oxide/Li/reduced graphene oxide (Li-rGO) using a spark reaction in densely stacked graphene oxide (GO) films to create uniform nanogaps, followed by the infusion of molten Li into the interlayer spacing (Fig. 5a)[88]. This electrode exhibited several notable advantages. Firstly, the layered rGO films with uniform nanogaps served as a stable 3D host that accommodated the large volume changes and facilitated the formation of a uniform and stable artificial SEI during charge and discharge processes. Secondly, the O-doping on the rGO surface improved its lithiophilicity and enhanced the Li intake capability of the composite electrode. The well-designed Li-rGO electrode demonstrated low dimensional variation (~ 20%), high capacity (~ 3 390 mAh g^{-1}), and low overpotential (~ 80 mV). Luo et al. employed an aerosol-assisted capillary compression approach to fabricating crumpled graphene balls with O-doping for stabilizing Li metal anodes[89]. The crumpled graphene balls exhibited a paper-ball-like structure and possessed several advantageous properties, leading to outstanding cycling stability (over 750 cycles) and desirable Coulombic efficiency (97.5%). The crumpled graphene balls provided excellent mechanical stability, enabling them to withstand dynamic volume changes without collapsing or fracturing. Additionally, the O-doping on the surface enhanced lithiophilicity and effectively regulated Li deposition behavior, while the high specific surface area inherited from graphene oxide reduced current density, thus preventing Li dendrite formation. Chen et al. prepared a controllable and porous nitrogen-doped graphene scaffold through chemical vapor deposition (CVD) using a nanoporous nickel template, aiming for an ultrahigh-rate lithium metal anode (Fig. 5b)[91]. When utilized as

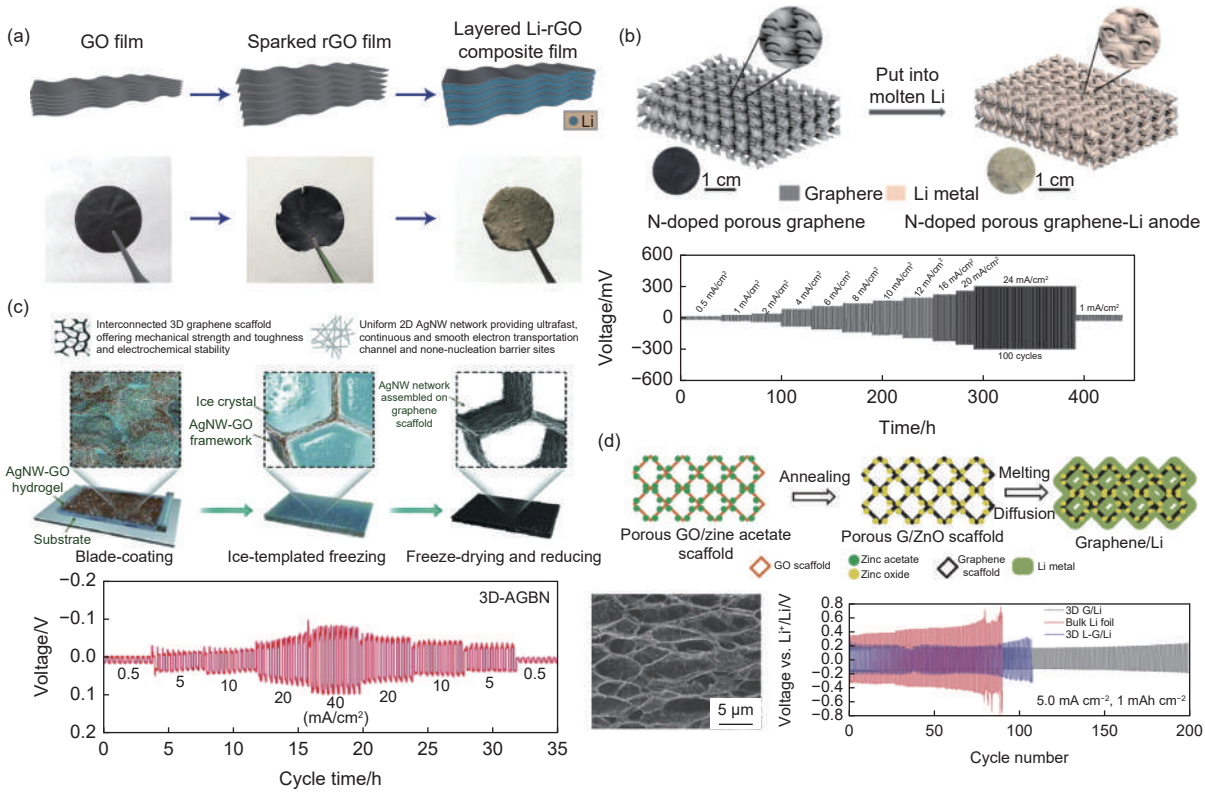

Fig. 5　(a) Schematic fabrication of a sandwich-like composite electrode film[88]. Reproduced by permission of Nature Publishing Group. (b) Fabrication process, and rate capabilities of the N-doped graphene–Li electrodes[91]. Reproduced by permission of Wiley-VCH. (c) Fabrication process, and rate performance of the hierarchical 3D-AGBN host[95]. Reproduced by permission of Wiley-VCH. (d) Fabrication process, SEM image and cyclic stability of the 3D G/Li anode[98]. Reproduced by permission of Wiley-VCH

an anode, this graphene scaffold exhibited exceptional combined performance, including ultrahigh rate capability of 36 mA cm^{-2} and long cycle life at 24 mA cm^{-2}. These achievements were attributed to the lithiophilic graphene scaffold with a large surface area, abundant porosity, and high conductivity. This scaffold not only inhibited Li dendrite growth by guiding Li deposition behavior but also accommodated the large volume change due to the open space within its well-designed structure. Zhi et al. stabilized Li metal anodes by designing a self-supporting fluorine-doped graphene-based host known as MGCN, wherein the fluorine doping facilitated the formation of a stable LiF-enriched SEI[92]. Leveraging the inherent advantages of graphene-based hosts, the MGCN electrode demonstrated a high Coulombic efficiency of 99% over 300 cycles.

Indeed, incorporating additional lithiophilic seeds and coatings can greatly enhance the wettability of graphene-based hosts/carriers with metallic Li. Here are a couple of examples: Braun et al. developed a composite electrode consisting of graphene and Au nanoparticles (AuNPs) for Li metal anodes, where the AuNPs were uniformly sandwiched by rGO films (Au-rGO)[93]. Due to the lower Li nucleation overpotential of AuNPs compared to rGO sheets, the AuNPs facilitated Li deposition between the rGO sheets instead of on the rGO surface. This arrangement effectively suppressed Li dendrite growth and allowed for through-plane thickness change, resulting in the formation of a stable SEI. The Au-rGO electrode demonstrated a decent capacity of 2 mA h cm^{-2}, a moderate Coulombic efficiency of 98%, and good cyclic stability over 1 600 h. Liang et al. prepared a hierarchical bi-continuous network comprising interconnected 3D graphene (3D-AGBN) and continuous silver nanowires (AgNW) as a confident host for Li metal anodes, achieving exceptional rate capability and cyclic performance (Fig. 5c)[95]. In this electrode design, the AgNWs with zero nucleation overpoten-

tial regulated the plating/stripping behavior of metallic Li, effectively suppressing Li dendrite growth. Simultaneously, the bi-continuous network with abundant porosity and a large specific surface area facilitated ultrafast electron transportation and accommodated the significant volume changes during charge/discharge cycling. Notably, when combined with a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode in a full cell configuration, the electrode exhibited excellent rate capability and outstanding cycling performance, surpassing 1 000 cycles even at 10 C. Besides, Liu et al. introduced a novel 3D graphene/Li metal composite anode (3D G/Li anode) by incorporating a cellular graphene/ZnO nanoparticles hybrid host and infusing molten Li, resulting in several notable advantages (Fig. 5d)[98]. First, the presence of ZnO nanoparticles enhanced the interaction between the graphene scaffold and metallic Li, promoting the formation of ultrathin Li layers that coated on the graphene scaffold. This Li coating significantly improved the reversibility of Li stripping and plating. Second, the cellular graphene scaffold, with its high specific surface area and conductivity, effectively reduced the current density, guiding Li plating/stripping behavior. Third, the available pore structure of the graphene scaffold endured the large volume change that occurred during the operation process, thereby minimizing mechanical stress on the electrode. The 3D G/Li anode demonstrated superb cyclic stability, enduring 200 cycles at 5 mA cm^{-2}. Moreover, the Li-ion capacitor cell based on the well-defined 3D G/Li anode exhibited enhanced performance in terms of impressive cycling performance (4 000 cycles) and superior rate capability (up to 30 A g^{-1}).

5 3D carbon frameworks-based hosts/carriers for lithium metal anodes

Three-dimensional (3D) carbon frameworks have garnered significant research attention due to their exceptional attributes, including high surface area, cost-effectiveness, facile synthesis, and tunable microstructure. These attributes make them highly desirable for advancing high-performance energy storage and conversion systems, particularly in the context of Li-S and Li-O_2 batteries[104–106]. In recent times, a series of scholarly investigations have emerged, focusing on the mitigation of Li dendrite growth and addressing the challenges associated with the substantial expansion of the electrode volume. This has been accomplished through the utilization of 3D carbon frameworks, with particular emphasis on biomass-derived structures and commercially available carbon cloth[107–109].

5.1 Biomass derived carbon

Biomass-derived 3D carbon frameworks represent a promising category of carbon frameworks that exhibit novel and distinctive microstructures inherited or evolved from raw materials. These frameworks have been extensively explored for their ability to design well-controlled electrodes in lithium metal batteries[107, 110–116]. Notably, natural wood has demonstrated remarkable potential in the creation of low-tortuosity and ordered carbonaceous hosts/carriers, owing to its vertically aligned channels along the growth direction. For instance, Li et al. developed a capillarity-involved low-tortuosity carbonaceous host (CTC) inspired by the structure of leaf veins, employing a simple annealing process followed by chemical vapor deposition[117]. In this design, carbon nanofiber mats were uniformly anchored on a self-supporting carbonized wood substrate, which featured vertically aligned micro-channels (Fig. 6). The resulting CTC electrode exhibited exceptional performance, including a high area capacity of 40 mAh cm^{-2}, extraordinary cyclic stability (1 080 cycles even at 10 mA cm^{-2}), remarkable rate capacity (40 mA cm^{-2}), and low voltage hysteresis (30 mV). The unique channel structure of the well-designed host facilitated efficient Li-ion transport throughout the electrode, while effectively tolerating volume changes during stripping and plating processes, thereby enabling uniform Li deposition. Moreover, the nanofiber mats enhanced the interaction between CTC and the electrolyte, promoting a uniform distribution of Li-ions and regulating Li nucleation behavior. Another notable example is the

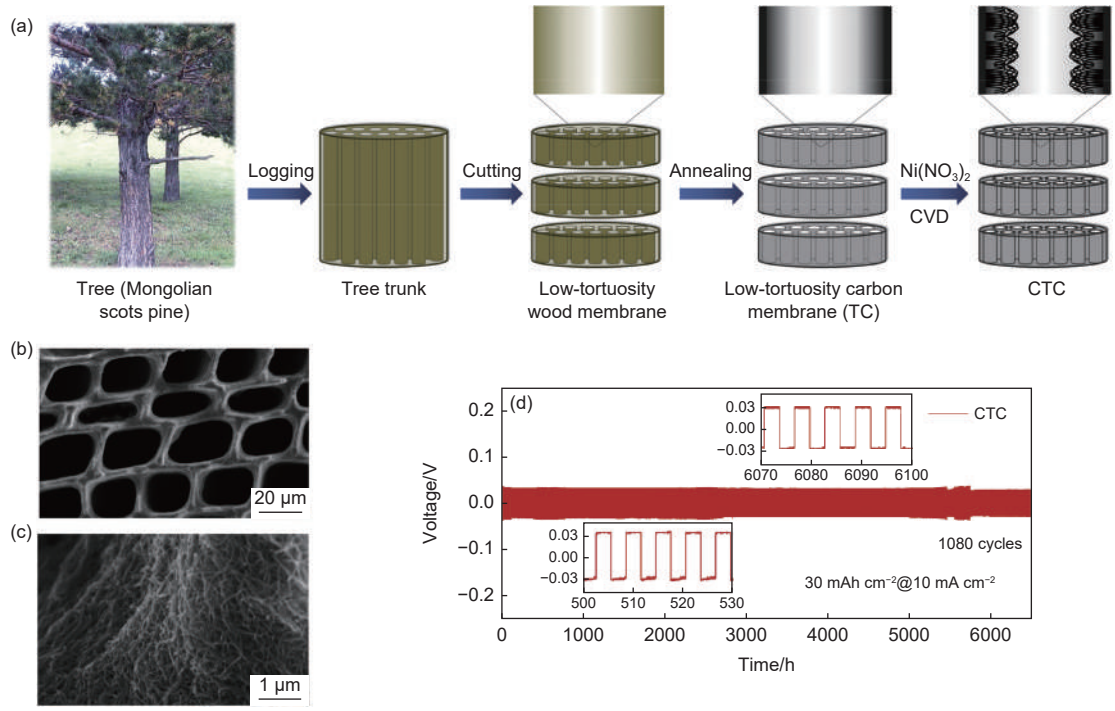

Fig. 6　(a) Fabrication process, (b-c) SEM images, and (d) cyclic stability of the CTC electrode[117]. Reproduced by permission of Elsevier

highly porous and wettable 3D conductive carbonized wood (C-wood) for Li metal anodes, reported by Hu et al.[108]. This material was synthesized through a 2-step process involving thermal annealing and a facile solution method to coat ZnO onto the wood template. The ZnO layer inherently enhanced the wettability of metallic Li on the C-wood, while the unique channel structure inherited from natural wood accommodated volume changes and modulated current distribution. Consequently, the C-wood electrode exhibited uniform Li deposition during charging and discharging processes. Symmetric cells constructed with the well-defined Li/C-wood anode demonstrated stable cycling performance (approximately 150 h at 3 mA cm^{-2}) and low voltage hysteresis (90 mV).

In addition to natural wood, other biomass sources have also been investigated for the design of carbonaceous hosts/carriers for Li metal anodes. For instance, Wan et al. demonstrated the conversion of commercial cotton into a 3D flexible hollow carbon fiber (3D-HCF) skeleton using a simple and scalable carbonization method under an Ar atmosphere[114]. The well-designed 3D-HCF structure provided storage space for metallic Li in the interspace between fibers and inside the hollow tubular fibers. This arrangement effectively regulated the deposition behavior of metallic Li and significantly reduced volume expansion. Furthermore, the commercial cotton precursor endowed the 3D-HCF with abundant active sites, enhancing its affinity for metallic Li. The 3D-HCF electrode exhibited excellent performance, including outstanding Coulombic efficiency of 99.5%, excellent cycling stability (over 1 200 h), and high areal capacity. Moreover, when integrated into a full cell with a $LiFePO_4$ cathode, the 3D-HCF electrode contributed to enhanced electrochemical performance.

5.2　Commercial carbon cloth

Commercial carbon cloth, composed of interwoven carbon fibers, offers several advantageous characteristics that make it well-suited for use in Li metal batteries. Its mechanical stability, good conductivity, favorable porous structure, and applicable specific surface area contribute to shortening the Li-ion transport path, adjusting electrode volume expansion, and minimizing current density[118–123]. Additionally, the flexibility of carbon cloth makes it a promising candidate for constructing self-supporting electrodes in high-performance Li metal batteries. For instance, Chen et al. utilized carbon cloth directly as an interface layer to protect against metallic Li deposition,

resulting in a dendrite-free composite anode known as Li@CC[117]. In this electrode architecture, carbon cloth played a crucial role in facilitating charge transfer, reducing current density, and accommodating volume variation, thereby inhibiting the growth of Li dendrites. The Li@CC electrode exhibited a low hysteresis (150 mV) and excellent cyclic stability (over 200 cycles). The full cell paired with the $Li_4Ti_5O_{12}$ cathode delivered stable cycling performance and remarkably rate capability.

Indeed, functionalized design of commercial carbon cloth is crucial to enable efficient regulation and guidance of uniform metallic Li deposition. Researchers have explored various strategies to modify commercial carbon cloth for enhanced performance in Li metal batteries. For example, Zhang et al. developed a design of N, P co-doping carbon cloth (NPCC) by thermally polymerizing polyaniline on the surface of carbon cloth in the presence of phytic acid (Fig. 7a)[119]. The 3D N, P co-doping carbon substrate exhibited significantly improved Li affinity, effectively regulating Li deposition behavior and inhibiting dendrite growth. When coupled with an iodine cathode, the Li-I_2 cell using NPCC demonstrated ultralong cyclic performance (up to 4 000 cycles) even at high rates (10 C) and favorable capacity (197 mAh g^{-1}). Lu et al. proposed a 3D multifunctional host, known as KNCC, by simultaneously etching and doping commercial carbon cloth[120]. The resulting KNCC electrode, with homogeneous defects and N-doping active sites, effectively controlled Li nucleation and growth and catalyzed the reduction of electrolyte, leading to the formation of Li_3N/LiF/N-O rich SEI. When employed in Li-$LiFePO_4$ batteries, the full cell exhibited outstanding rate capability and superb capacity retention (typically 86% after 500 cycles). In another study, Liu et al. developed a self-supporting carbon cloth substrate covered with tent-like N-doping porous carbon microcavities (NPCM@CC) through a facile carbonization process using a SiO_2 template (Fig. 7b)[121]. The NPCM@CC electrode displayed exceptional metallic Li storage properties, including high coulombic efficiency (99.1%), remarkable cycling performance (over 4 200 h at 1 mA cm^{-2}) and ultralow voltage hysteresis (46 mV). The well-ordered tent-like microcavities on the 3D carbon cloth provided a high specific surface area, preventing Li^+ aggregation and regulating Li deposition behavior. Moreover, nitrogen doping in the NPCM@CC electrode enhanced the lithiophilicity of the carbon substrate, reducing nucleation overpotential and inhibiting dendrite growth.

In addition to doping strategies, another effective approach to enhancing the lithiophilicity of carbon cloth substrates is the introduction of lithiophilic seeds and coatings, such as Au, Ag, ZnO, TiO_2, VN,

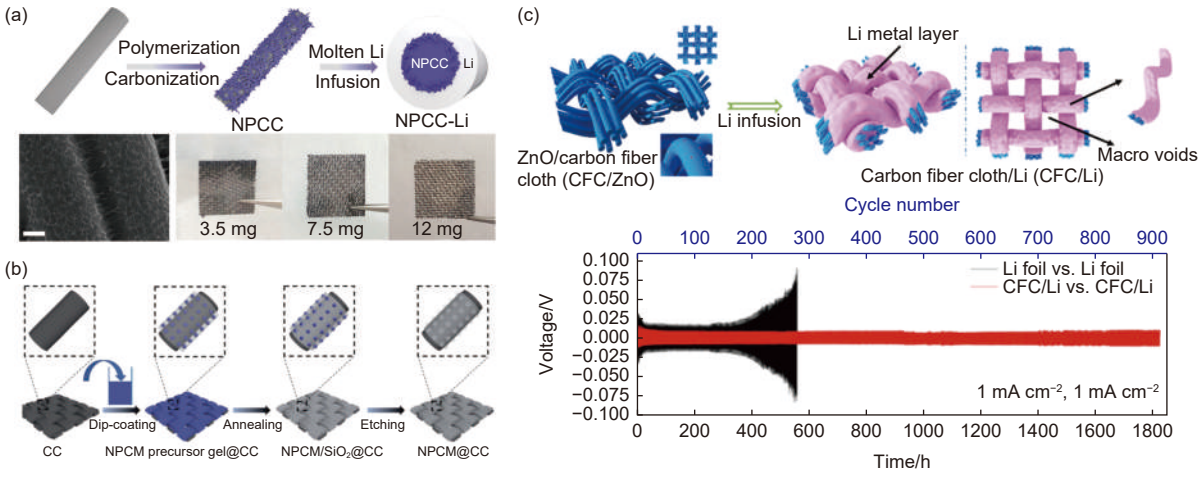

Fig. 7 (a) Fabrication process, SEM image, and photographs of the NPCC-Li electrode[119]. Reproduced by permission of Wiley-VCH. (b) Preparation process of the NPCM@CC[121]. Reproduced by permission of the Royal Society of Chemistry. (c) Synthetic process and cyclic stability of the CFC/Li electrode[123]. Reproduced by permission of American Chemical Society

and more. These seeds and coatings promote favorable interaction between the carbon cloth substrate and metallic Li. For example, Rosei et al. improved the lithiophilicity of activated carbon cloth by uniformly dispersing single-cluster Au. The electrodeposition of Li on these single-cluster Au sites, with zero overpotential, significantly enhanced the affinity between the carbon cloth substrate and metallic Li. The resulting electrode exhibited remarkable cycling stability and superior deep cycle performance[122]. Liu et al. proposed a design of a ZnO-decorated carbon fiber cloth/Li hybrid anode (CFC/Li) by pre-infusing metallic Li into the microchannels of carbon fiber cloth covered with a ZnO coating (Fig. 7c). The 3D interconnected channels of the carbon fiber cloth regulated and guided Li plating behavior, confining Li deposition within the microchannels. The high conductivity of the carbon fiber cloth provided sufficient electrons for Li deposition, effectively preventing the formation of Li dendrites. As an anode, the CFC/Li electrode demonstrated outstanding cycle stability (1 800 h at 1 mA cm^{-2})[123].

6 Conclusion

The ever-increasing demand of lithium batteries with longer cycle life, as well as higher power and energy density has stimulated a surge in developing practical Li metal anodes. Recently, carbon hosts/carriers with various structures and/or dimensionalities has been applied to solve the tough obstacles, and significant breakthroughs have been made. In this review, we have elaborated the recent experimental advances reported on carbon host/carrier in developing Li metal anodes based on dimensional variations of carbon units. For different dimensionalities of carbon units, a serious of strategies for enhancing compatibility between carbon hosts/carriers and Li metal have been intensively presented to decrease the Li nucleation barrier and guide reversible Li plating/stripping. By contrast, these effective strategies can indiscriminately enhance the affinity of carbon units with various dimensionalities towards metallic Li. In addition, dimensional feature plays a key role in the controllable design of 3D hierarchical carbon hosts/carriers. 0D carbon nanospheres usually require additional binders and collectors toward the construction of Li metal hosts/carriers. Different from 0D carbon nanospheres, 1D and 2D carbons exhibit great potential in designing 3D self-supporting hierarchical carbon hosts/carriers for metallic Li. In comparison with 1D carbon nanotubes/fibers, 2D graphene-based hosts/carriers typically intake metallic Li and effectively avoid the connection with electrolyte, thereby benefiting the formation of stable artificial SEI layers. For low-cost 3D carbon frameworks, the well-designed carbon hosts/carriers based on 1D and 2D carbon units show diversiform and controllable structures. On the basis of outline aforementioned, a unique and novel insight into constructing carbon hosts for the development of other emerging alkali metal anode has also been inspired.

7 Prospectives and challenges

While a variety of efforts has significantly improved the electrochemical performance of Li metal anodes, there are still several vital challenges that imperatively need to be solved for accelerating the future commercialized application of LMBs.

First, Li metal composite anodes must be stored/used in argon-filled glovebox or drying room duo to its atmospheric corrosion. Improving the tolerance of Li metal anodes to humid atmosphere is one of the keys to effectively reducing the manufacturing cost and improving the safety of LMBs, but scrupulous studies should be strengthened.

Second, although few efforts in designing hierarchical hosts/carriers have provided fast electron/ion transport pathway to boost good rate capability of Li metal anodes, the ultrahigh rate performance achieved remains a crucial challenge. Thus, research works should pay more attention to simultaneously obtain ultrahigh rate and stable electrochemical performance of the electrode for meeting the perceived inconvenience of charging.

Third, several above-mentioned flexible and self-supporting carbon hosts/carriers have significant ap-

plication potential in flexible energy storage devices, but the interaction between carbon hosts and Li metal is indefinable under bent and folded conditions. Thus, more efforts should be made to reveal the dynamic interfacial action mechanism to guide the construction of flexible composite anode.

Fourth, the amount of Li deposition in a well-designed electrode is also a vital factor in assessing its feasibility for real battery applications. While tremendous efforts have been developed to meet the troublesome problems of Li metal anodes, the problem of Li overload during the preparation needs urgent attention.

Fifth, carbon hosts with meticulous design have achieved great progress for Li metal anodes in the current research, but the large-scale preparation of these well-designed carbon hosts remains a huge challenge.

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