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Advanced design strategies for multi-dimensional structured carbon materials for high-performance Zn-air batteries

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Abstract: Zn-air batteries (ZABs) featuring high safety, low-cost, high specific capacity and environmentally friendliness have attracted much attention and emerged as a hot topic in energy storage devices. However, the sluggish kinetics of the oxygen evolution/reduction reactions (OER/ORR) at the air electrode and the non-negligible dendritic growth at the anode have hindered their large scale applications. Carbon materials with low-cost, good electrical conductivity, chemical stability and bifunctional OER/ORR activities have been widely studied for ZABs in the past few years. This review begins with a discussion of the basic working principle of ZABs, followed by an introduction of various carbon materials which focuses on their roles and superior properties in the applications of ZABs. This review also discusses the essential roles of multi-dimensional carbon materials as major components of ZABs, i.e., air electrodes, zinc anodes and separators, in improving the performance of ZABs. Finally, prospects for the future use of carbon materials to improve ZAB performance are explored.

Key words: Multi-dimensional carbon; Zn-air battery; Oxygen reduction reactions; Zn anode; Separator

1 Introduction

Facing ever-increasing demands in energy and growing environmental pollution caused by the heavy usage of fossil fuels, it is remarkably significant to develop clean sustainable energy sources like wind, solar, tide, etc[1,2]. However, their electricity-output is intermittent and largely associated with geographical condition, which propels and accelerates the development of energy conversion and storage technologies. With the benefits of high theoretical energy density (1 086 Wh kg^{-1})[3,4], inherent safety, environmentally friendliness, affordable cost, zinc-air batteries (ZABs) are considered as one of the most potential candidates for next-generation energy devices and have received special interest recently[5–7].

Typically, the ZABs are composed of an air electrode with a sandwich-type structure of a catalyst layer, current collector and gas diffusion layer, a Zn anode, a separator and alkaline electrolyte. Much effort has been devoted to exploring each component of ZABs and the recently reported ZABs have achieved excellent performance in lab such as extremely high maximum power density (~168.3 mW cm^{-2})[8] and long-life span (even to 1 600 h at 5 mA cm^{-2})[9,10]. Despite this, large-scale commercialization is still a huge challenge facing current ZABs due to the sluggish kinetics of oxygen reduction/evolution reactions (ORR/OER) in air electrodes[11–13], poor reversibility of Zn anode[14–17] and low chemical/mechanical stability of separators[18–20]. It is generally known that carbon materials have excellent electrical conductivity, low-cost, adjustable structures and properties. Various modification strategies such as heteroatom doping, vacancy engineering, dimensional regulation and compositing, have been extensively studied in ZABs. Carbon materials can be used as conductive porous

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catalyst carriers for exposing more active sites and rapid electron transfer[21], which can be surface-decorated on Zn anode by benefit of high specific surface area for alleviating the passivation[22], or can be rationally designed as separators with suitable porosity and high mechanical strength for fast ion transport and avoiding internal short-circuit under external stress. Considering that several efforts have been taken as seminal works and the numerous advancements in this field, it is urgent to systematically summarize the modification methods of carbon materials and their applications in ZABs.

In this review, we summarize the recent progress of carbon materials in different components of ZABs including air electrodes, zinc anode and separators (Fig. 1). The dimensional and structural advantages as well as the preparation methods of carbon materials are introduced and the mechanisms for battery performance enhancement are deeply discussed. Finally, we present the opportunities and challenges of carbon materials applied in ZABs.

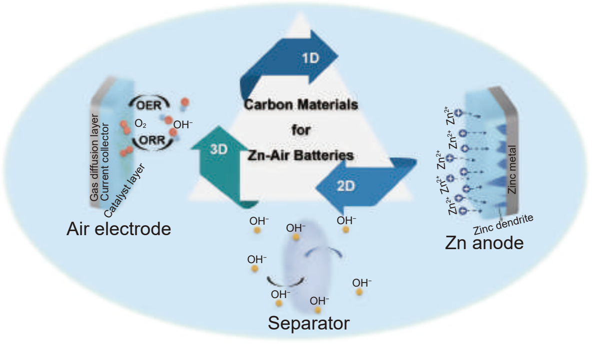

Fig. 1 Multi-dimensional carbon materials in Zn-air batteries.

2 Strategies for high-performance air-electrode by multi-dimensional carbon materials

The slow kinetic processes of ORR and OER limit the energy conversion efficiency of ZABs severely. Thus, the main demand for air electrodes is high activities towards ORR and OER to lower their overpotentials and structural robustness to achieve long-term durability[23]. Compared with commercial noble metal-based electrocatalysts, carbon materials not only exhibit affordable cost and favorable catalytic activity, but also have multifunctionality served as conductive supports and catalytically active sites. Based on the above considerations, carbon materials have received considerable attention as electrocatalysts of air electrodes in ZABs.

The apparent activity of a material is related to the intrinsic activity of individual sites and the density of available active sites. The apparent morphology has an impact on the specific surface area, active site density, material hydrophobicity and the stability of electrode materials[24], while the microstructure directly affects the intrinsic activity and stability of individual sites[25]. Therefore, the design of catalytic materials needs to fully consider the morphology, components and structure to synergistically enhance the catalytic activity and stability, which can tremendously contribute to obtaining high-performance ZABs.

Carbon nanostructures are divided into one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) carbon nanostructures based on their dimension. Based on previous studies, the density of active sites, intrinsic activity and efficient electron/ion transport is necessary to achieve excellent catalytic activity of ORR/OER. In general, 1D carbon materials with a uniform structure possess superior electrical properties and strong tolerance to stress change, showing superiority towards ion diffusion and electron transport[26]. The ultra-thin thickness, large lateral size and unique layered structure of 2D carbon materials can expose abundant and easily available catalytic active sites[27]. 3D carbon materials with continual and adjustable porous structures afford fast electronic delivery channels[28]. Thus, carbon materials with different dimensions show unique abilities in improving the ORR/OER performances.

2.1 One-dimensional carbon materials

1D carbon materials, such as carbon nanotubes and carbon nanofibers, are widely used in air electrodes due to their large aspect ratios and small diameters[29]. The morphological and structure features of 1D carbon materials lead to unique physicochemical features like large specific surface area, good mechanical properties and axially fast channels for direct electron conduction. Therefore, 1D carbon materials are recognized as one of the most promising materials for the air electrode of ZABs[30]. For instance, Xia et al. developed a N-doped carbon nanotube matrix (NCNTM) as a bifunctional oxygen electrocatalyst by two-steps annealing (Fig. 2a). N doping plays an essential role in the modulation of carbon materials. N doping not only reduces lattice mismatch, but also provides a significant enhancement for ORR[31]. The special interconnected structure was obtained by the pyrolysis of carbon skeletons surface-coated with ZIF-67 in the reductive atmosphere. Benefiting from the synergic effect of sufficient metal-nitrogen-carbon sites and continual porous network structure, it exhibited excellent activities for oxygen electrocatalysis. Moreover, NCNTM-based ZAB delivered an outstanding cycling stability over 1 600 h at a current density of 5 mA cm^{-2} (Fig. 2b)[32]. Besides, Carsten Streba and his co-workers fabricated a class of bimetallic Mn/V functionalized N, S co-doped carbon nanotube composites. The N, S co-doped CNTs could provide fast electron transport channels and promote the conductivity and catalytic activity remarkably. The functionalized N, S co-doped carbon nanotube composites exhibited excellent performance in ORR and OER (OER: over- potential: 360 mV at 10 mA cm^{-2}, ORR: E_{onset} of 0.95 V; $E_{1/2}$ of 0.84 V) and high stability, which is comparable to the commercial Pt/C (20%) catalyst[30]. To further enhance their electrocatalytic activity, 1D carbon materials are normally blended with other catalytically active materials (e.g. transition metal nanoparticles[33], metal oxides[34], LDHs[35]). In this regard, our group embedded CoSe$_2$ nanoparticles in nitrogen-doped carbon nanosheet array penetrated with carbon nanotubes (CoSe$_2$-NCNT NSA) as an electrocatalyst. 1D N-doped CNTs were interwoven between the nanosheets and formed a "cactus" hybrid electrode (Fig. 2c). Interestingly, owing to the unique array structure and the interwoven of the 1D CNTs, the electrode and electrolyte were contacted firmly even the flexible battery was deformed by external forces (Fig. 2d). In addition, the CoSe$_2$-NCNT NSA-based flexible battery showed stable charge-discharge performance at variable temperatures from 0 to 40 °C and could work stably at different angles from 0° to 180° (Fig. 2e)[36].

The large aspect ratio is a characteristic that makes the 1D carbon materials prone to agglomeration, and unmodified 1D carbon materials suffer from the lack of reactive groups. Currently, it was found

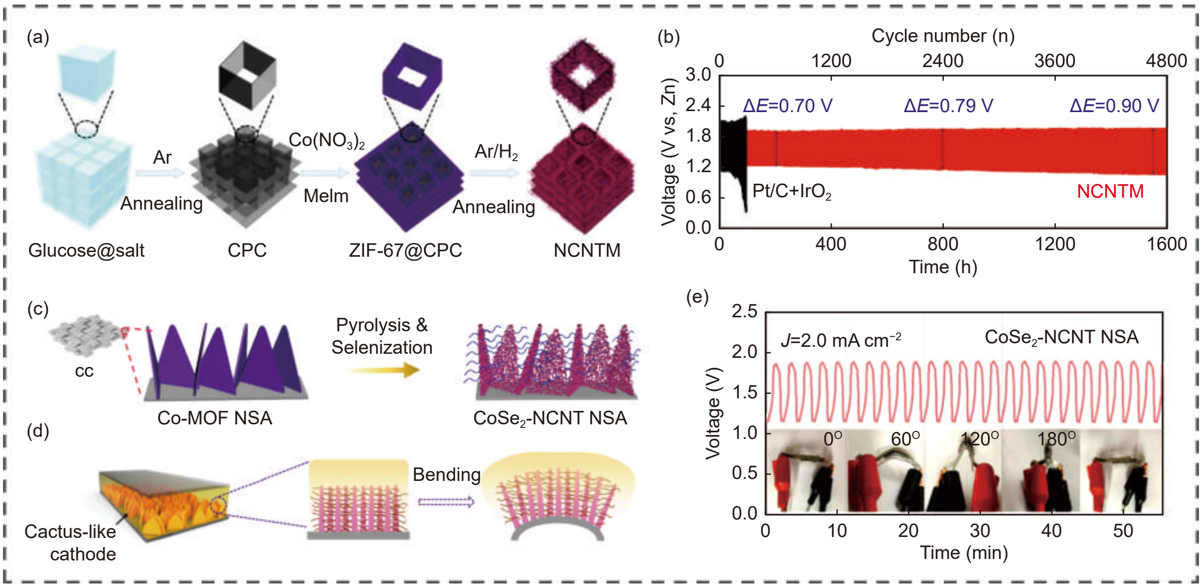

Fig. 2　(a) Schematic images of NCNTM. (b) Galvanostatic cycling stability at 5 mA cm^{-2} for NCNTM and Pt/C+IrO$_2$ assembled ZABs[32]. (c) Schematic of the CoSe$_2$-NCNT NSA. (d) The cactus-like electrode for flexible ZABs under flat and bending states. (e) Cycling performance of the CoSe$_2$-NCNT NSA-based flexible ZAB at different bending angles[36] (Reprinted with permission).

that advanced design methods can effectively control the structure, morphology and composition of materials to acquire the high-performance catalyst. A series of 1D carbon materials such as single-walled/multi-walled carbon nanotubes[37,38], carbon nanobelts[39,40] and graphite nanorods[41] have been produced by chemical vapor deposition (CVD). Besides, the template-assisted method with good controllability and stability have been widely reported in the preparation of 1D carbon materials[42,43]. In this section, the advancement of these two preparation methods is mainly summarized.

The 1D carbon materials prepared by CVD possess the advantages of high yield, controllable structure, abundant defects. Hence, CVD has emerged as an advanced design strategy for the synthesis of 1D carbon materials. In general, the mechanism of CVD for the preparation of 1D carbon materials includes two steps, firstly the catalytic decomposition of hydrocarbon gases and then the carbon radicals assembled into 1D carbon materials. CVD can be operated at a low temperature and pressure under catalysis of some transition metals or their alloys. As a typical example, Huang et al. constructed a Se-doped CNT-based FeCo bifunctional catalyst (FeCo/ Se-CNT) with high exposed active area by the gravity guided CVD method (Fig. 3a). The CNTs fabricated by this advanced design strategy is longer, thinner and more uniform. Meanwhile, the size and length of CNTs can be controlled by adjusting the amount of melamine. As a result, the rechargeable liquid and flexible all-solid-state ZABs based on FeCo/Se-CNTs demonstrated high peak power densities of 173.4 and 37.5 mW cm^{-2}, respectively (Fig. 3b)[44]. Besides, Wolfgang Schuhmann et al. achieved the conversion of cobalt boride (CoB) by direct CVD growth of NCNTs on the surface of CoB (CoB/NCNT, Fig. 3c-d), where the CoB nanoparticles served as both the matrix and catalyst for the growth of NCNTs. It was found that CNTs with different diameters and thicknesses could be controlled by designing the temperature of the CVD method. Notably, the pronounced OER activity was ascribed to the enhancement of electric conductivity of the catalyst layer and highly distributed CoB species after the CVD process. In addition, ZABs assembled with CoB/NCNTs exhibited wonderful durability of 170 cycles at 10 mA cm^{-2}[45].

The template-assisted method is another efficient preparation strategy for 1D carbon materials with designable composition and morphology. Nor-

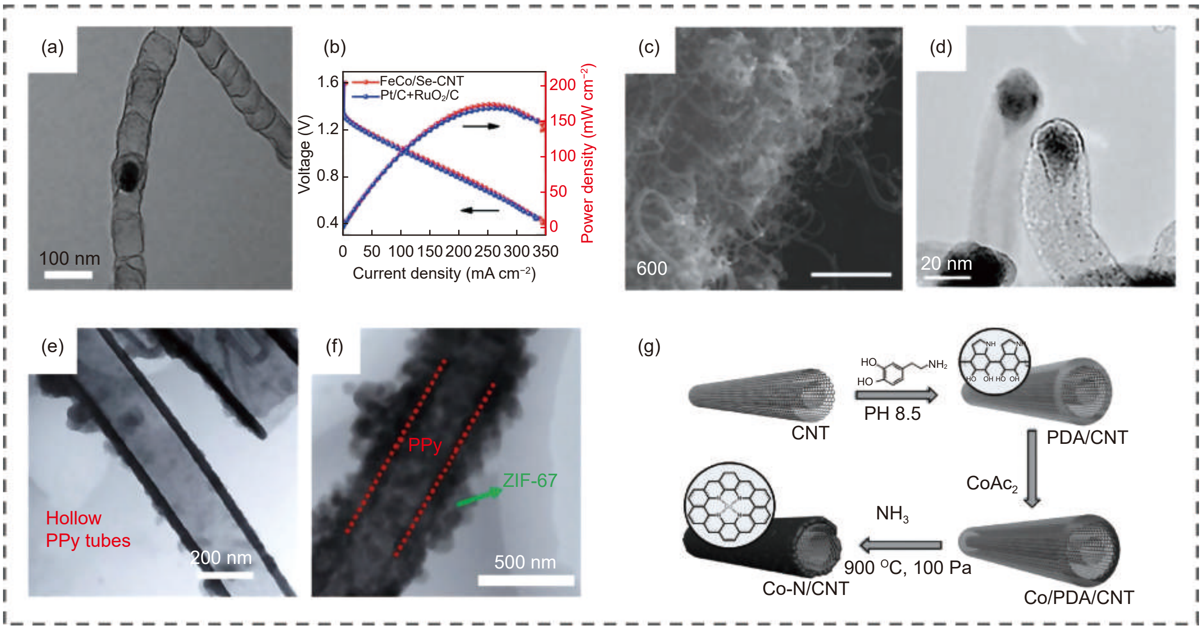

Fig. 3 (a) HR-TEM image of the FeCo/Se-CNT catalyst. (b) Discharge polarization and corresponding power density curves[44. (c) SEM image of CoB/NCNT bifunctional electrocatalysts prepared at different temperatures. (d) TEM image of individual CNTs and encapsulated CoB nanoparticles[45]. (e) TEM image of PPy nanotubes. (f) TEM image of PPy@ZIF67[50]. (g) Schematic synthetic procedure of Co-N/CNTs[51] (Reprinted with permission).

mally, the suitable templates are highly crucial to achieve controllable synthesis of 1D carbon materials. Various templates such as halloysite, palygorskite, and silica nanotube were used to prepare the fixed size CNTs[46,47]. Moreover, the self-sacrificing templates like PANI[48] and PAN[49] can be served as precursors to form 1D carbon nanofiber assembly structure after direct carbonization. Recently, Chen et al. embedded Co nanoparticles in hollow N-doped carbon tubes (Co@hNCTs) through a simple template-assisted method (Fig. 3e). The surfactant-modified polypyrrole (PPy) nanotubes served as the architecture-guided templates efficiently trap Co^{2+} for *in-situ* growth of ZIF-67 on PPy nanotubes (Fig. 3f). As a result, as-synthesized catalyst used as an air electrode in ZABs showed a high peak power density of 149 mW cm^{-2} and good stability[50]. Li and co-workers used CNTs as a template to prepare a carbon-nanotubes supported Co-N/C core-shell hybrid material (Co-N/CNT) by self- polymerization and high-temperature pyrolysis (Fig. 3g). The Co-N/CNTs exhibited an outstanding half-wave potential of 0.91 V and excellent stability. Moreover, the maximum power density of Co-N/CNT-based ZAB reached 300 mW cm^{-2}, demonstrating the essential role of graphitic CNTs[51].

2.2 Two-dimensional carbon materials

The successful preparation of graphene in 2004 opened a new era of 2D carbon materials. Generally, carbon materials with a single layer or several layers, whose thickness is far less than transverse size, are defined as 2D carbon materials[27,52]. The ultra-thin thickness, large transverse size, unique layered structure and large specific surface area of 2D carbon materials provide abundant and accessible catalytic active sites[53] and excellent electrical conductivity for efficiently enhancing the charge transfer ability. Therefore, 2D carbon materials with advanced design can promote the diffusion/permeation process in the triple-phase interfaces (solid catalysts-oxygen gas-liquid electrolyte) of air cathode and improve the performance of ZABs significantly.

Graphene, as the most high-profile 2D carbon materials, is composed of a sp^2 hybridized hexagonal honeycomb carbon structure with the carbon-carbon distance of 0.142 nm[54]. Whereas, graphene has negligible catalytic activities towards oxygen catalytic reactions. The theoretical and experimental results showed that heteroatom doping and vacancy engineering can effectively improve the catalytic performance of graphene-based materials. Heteroatom dopants in graphene affect the charge density distribution and form topological defects, which effectively modulate the band gap of graphene by making defects on graphene. Graphene with vacancy engineering exhibits a metal-like electronic structure. Thus, heteroatom doping and vacancy engineering are effective to improve the electrochemical performance for graphene[55]. For instance, Diao et al. anchored 2D ultra-thin graphene onto Cu-doped Co_2P nanoparticles closely, which significantly expose the surface actives sites and enhance efficient mass and charge transport (Fig. 4a). Consequently, the assembled flexible solid-state ZABs offered a high maximum power density of 52.5 mW cm^{-2} and good stability of 32 h[56]. Similarly, Li and co-workers synthesized a bifunctional iron/nitrogen co-doped graphene (2D Fe-NG) catalyst by pyrolyzing as-prepared 2,5-benzimidazole (ABPBI) and iron precursor (Fig. 4b). Furthermore, 2D Fe-NG-based ZABs demonstrated a high peak power density (235.2 mW cm^{-2}) and wonderful rechargeable capability[57]. Besides, graphene is a premium substrate to be combined with numerous non-noble metal catalysts. Typically, Shi et al. fabricated the graphene wrapped CoFe alloy (C/CoFe) by pyrolyzing a homogeneous precursor containing cobalt, iron ions and nitrogen-doped carbon quantum dots. The micropores and mesopores of the graphene provide more active sites and enable more uniform and faster mass and electron transport. Remarkably, the secondary ZABs delivered outstanding stability in long-term over 20 000 charge-discharge cycles since the obtained carbon layers can protect CoFe alloy nanoparticles from inactivation under the harsh environment[58].

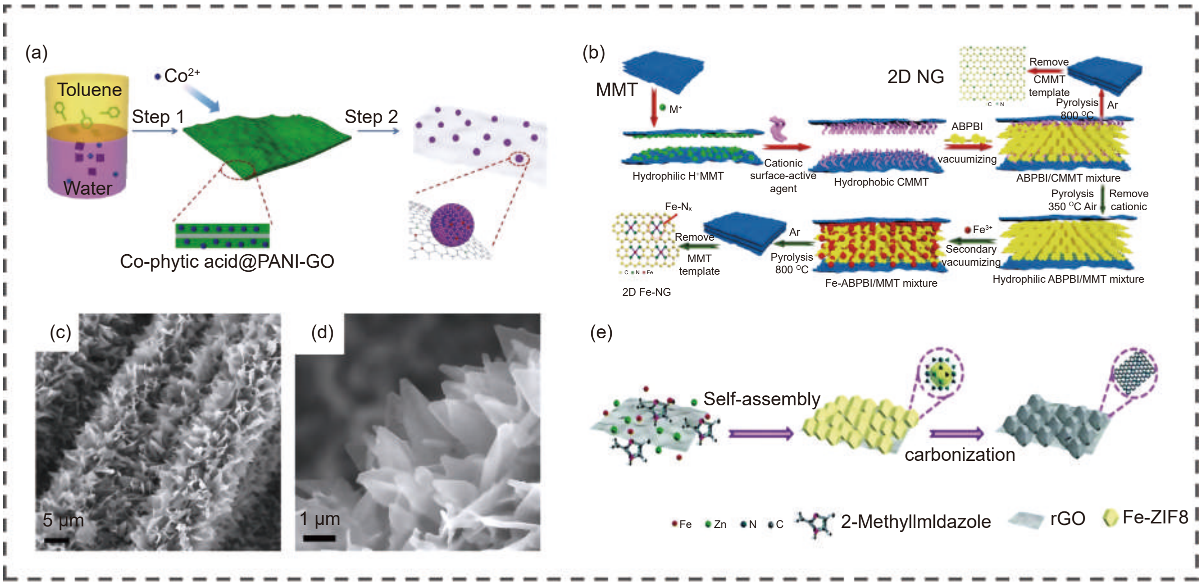

Fig. 4　(a) Schematic illustration of the fabrication process of Cu-Co_2P@2D-NPC[56]. (b) Preparation routes of the 2D NG and 2D Fe-NG[57]. (c-d) SEM images of NC-Co SA[62]. (e) Schematic illustration of the Fe-N-C/rGO catalyst synthesized by in situ Fe-doped ZIF-8 on reduced graphene oxide[63] (Reprinted with permission).

Alternatively, metal-organic frameworks (MOFs)-derived 2D carbon materials possess tunable pore size, large specific surface area, diverse skeleton structures and adjustable physical/chemical properties, which benefit for high-performance electrocatalysis[59–61]. For instance, Pennycook et al. used Co-MOF as a precursor to construct a hybrid electrode comprising Co single atoms anchored on porous N-doped carbon nanosheet arrays (Fig. 4c-d). The presence of Co single atoms endowed the catalyst with a low OER overpotential and high ORR saturation current. Meanwhile, the outer carbon shell reduces direct contact of wrapped Co nanoparticles with oxygen and prevent them from being oxidized. Besides, the assembled ZABs showed a high open circuit potential (1.411 V) as well as good cycling stability (2 500 min, 125 cycles)[62]. Zhao et al. constructed a Fe-N-C/rGO catalyst by covering the rGO surface with a uniform layer of Fe-doped ZIF-8-derived carbon particles (Fig. 4e). Thanks to the ingenious hierarchical structure, the mixture of Fe-doped ZIF-8 particles and rGO avoided particle aggregation, which enabled the catalyst with abundant electroactive sites for both ORR and OER[63].

Developing efficient approaches for the synthesis of 2D carbon materials with controllable composition and morphology is extremely important. Designing 2D materials into specific morphologies through some advanced design strategies, and in some cases, the materials into specific morphologies through some advanced design strategies, and in some cases, the addition of functional groups or metal elements can enhance the performance of Zn-air batteries successfully. To date, researchers have developed a variety of methods such as liquid exfoliation[64], mechanical cleavage[65], wet-chemical syntheses[66], and CVD[67]. Overall, these methods can be divided into two categories: “top-down” and “bottom-up” methods[68,69].

The top-down approach converts macroscopic carbon materials into ultra-thin (atomic scale) nanosheets and other morphologies through advanced design strategies, such as ball milling, liquid-phase exfoliation and physical vapor deposition[20–21, 70–72]. For instance, Zhang and co-workers applied advanced design strategies by H_2-etching to obtain the porous graphene *in-situ* on the surface of carbon fibers. Porous graphene sheets with ca. 300 nm thickness (Fig. 5b) were exfoliated directly on the surface, where some macropores with abundant oxygen-containing groups and defects were used as active sites

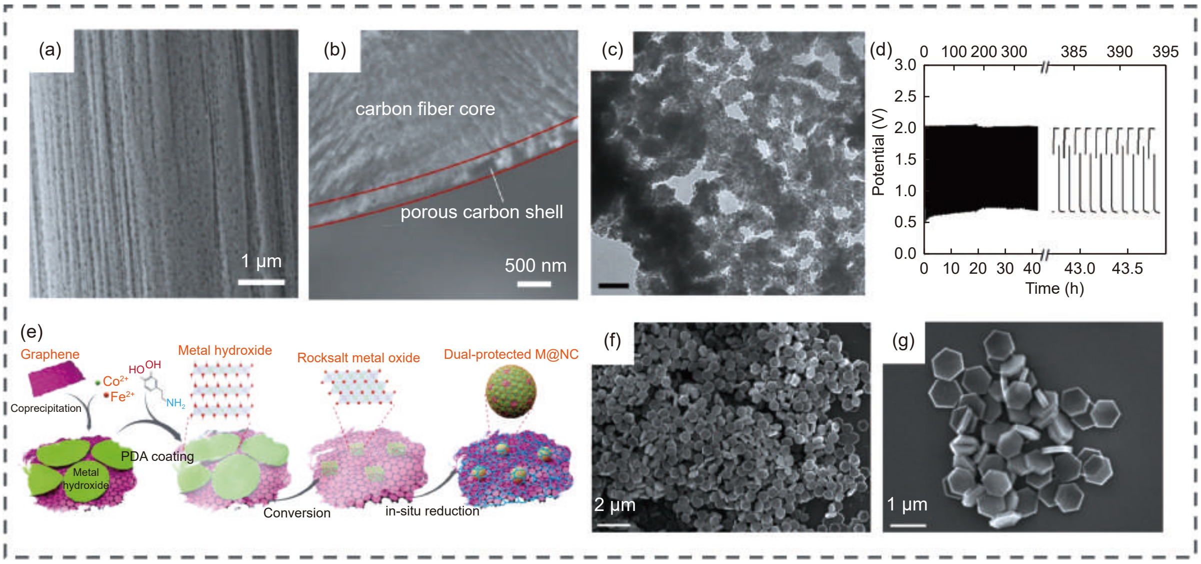

Fig. 5　(a) SEM image of O-CC-H_2. (b) SEM image of a cross section of o-CC-H_2[64]. (c) TEM image of CoS_x@PCN/rGO. (d) CoS_x@PCN/rGO in a rechargeable ZAB at a current of 50 mA[73]. (e) Synthesis and structural characterization of Co_2Fe@NC[78]. (f-g) Schematic illustration for the HXP preparation[76] (Reprinted with permission).

(Fig. 5a). Thus, the OER and ORR current densities of the graphene modified carbon fibers were 20 and 3 times higher than original carbon cloth, respectively[64]. Yang and co-workers synthesized a CoS_x@PCN/rGO catalyst by exfoliating porous carbon nitride (PCN) and subsequently mixing with graphene oxide (GO). Attributing to the internally accessible nitrogen sites and the porous structure (Fig. 5c), CoS_x@PCN/rGO -based ZABs achieved 394 discharge/charge cycles over 43.8 h (Fig. 5d), which is more stable than the commercial Pt/C catalyst[73].

The “Bottom-up” method can be used to obtain 2D carbon nanosheets with high aspect ratios by controlling the growth direction of nanosheets, which can limit the vertical scale[73–75]. This method is mainly used for the direct growth of 2D crystals under specific conditions and usually requires the assist of surfactants or inhibitors[76,77]. Tang et al. applied a CVD method to achieve a high density of metal nanoparticles completely wrapped in highly-graphitized carbon layers and immobilized by an external porous carbon network. Attributing to a dense distribution of highly active sites, the structure with a Co_2Fe_1 alloy core (Co_2Fe_1@NC) demonstrated excellent bifunctional electrocatalytic activity and exhibited a peak power density of 423.7 mW cm^{-2} when used as a cathode for ZABs (Fig. 5e)[78]. The “Bottom-up” method can keep the morphology of nanosheets intact through the advanced design strategy. Lin and co-workers synthesized a hexagonal 2D MOFs-derived carbon material with a topology-guided bottom-up method, which is a promising method to obtain 2D materials with complete architecture and regular shapes at their genesis (Fig. 5f-g). Furthermore, the catalyst demonstrated a low OER overpotential of 307 mV at 10 mA cm^{-2}[76].

2.3　Three-dimensional carbon materials

3D carbon materials have been intensively investigated as good support for catalysts in air electrodes. Generally, their multi-dimensional networks with abundant active sites on edges[79,80] can endow them with excellent conductivity[81,82] and high electrocatalytic activity. The advanced design of the hierarchical pore structure for 3D carbon materials makes them easy to achieve the rapid diffusion of reactants/products during electrocatalysis[83,84].

Hierarchical interconnected pores and conductive paths in the 3D porous carbon materials facilitate mass and electron transfer in electrocatalysis[85,86]. Porous structures play a critical role in regulating the exposure extent of active sites and diffusion of electrolytes. Specifically, macropores provide efficient mass transfer pathways[87,88], and meso/micropores provide a large surface area, increasing the accessibility of reactants to active sites and the number of active sites[89]. Liu et al. built a necklace-like carbon fibrous architecture with hierarchical porosity (Fe-P/NHCF). The prepared carbon nanofibers had hollow macro/mesopores structures (Fig. 6a), and the Fe-N/Fe-P double active sites were uniformly doped in the flexible carbon nanofibers (Fig. 6b). Attributed to the porous structure and double active sites, the portable solid-state ZABs based on Fe-P/NHCF displayed an open circuit voltage of 1.32 V and a peak power density of 42 mW cm^{-2}[90]. 3D hierarchical macrosheets consisting of *in situ* cobalt-catalyzed N-doped CNTs (Co@NCNTHMS) interconnected with each other were fabricated by Zhang and co-workers (Fig. 6c). Remarkably, the homemade ZAB based on the Co@NCNT HMS catalyst delivered a maximum power density of 159.83 mW cm^{-2} and a high specific capacity of 675.8 mA h g^{-1}[91]. Sun's team prepared an efficient electrocatalyst with Fe-N-C sites embedded in 3D N-doped mesoporous carbon framework (Fe-N-C/N-OMC). The Fe-N-C/N-OMC showed a comparable ORR activity to the Pt/C catalyst in an acidic electrolyte due to the slit micropores of carbon materials, which provide a space for the formation of FeN$_4$-C catalytic sites[92]. Hou et al. achieved morphological control of the core@shell MOFs by varying the Fe^{3+} content and constructed a 3D open carbon cage structure (Fig. 6d). The guest Fe^{3+} was introduced into an open carbon cage and self-assembled into a 3D structure of interconnected CNTs (Fig. 6e). Such hierarchically porous structures are beneficial for the accessibility of the electrolyte to internal pores, thus ensure rapid diffusion of the reactants/ intermediates/products for catalysis[93]. Wu et al. constructed a carbon aerogel with a 3D honeycomb nano-structure as a bifunctional cathode (Fig. 6f-g). As-prepared carbon aerogel exhibited excellent mechanical stability for bending and compression, as well as porous structure stability for bending and compression, as well as pores for efficient gas/ion diffusion[94].

The excellent properties of 3D materials endow them with great research prospects in ZABs. The unmodified 3D carbon materials have an inert surface and low reactivity. By advanced design strategies (appropriate templates, functionalization modifications, etc.) the morphology and structure can be prepared controllably, which can further improve the electrochemical properties of carbon materials and play a vital role in the performance enhancement of ZABs. With the purpose of obtaining 3D carbon materials, the synthesis methods mainly fall into two sorts: the template method and assembly method. It's investigated that template methods can easily control the microstructure and composition of the subsequent 3D

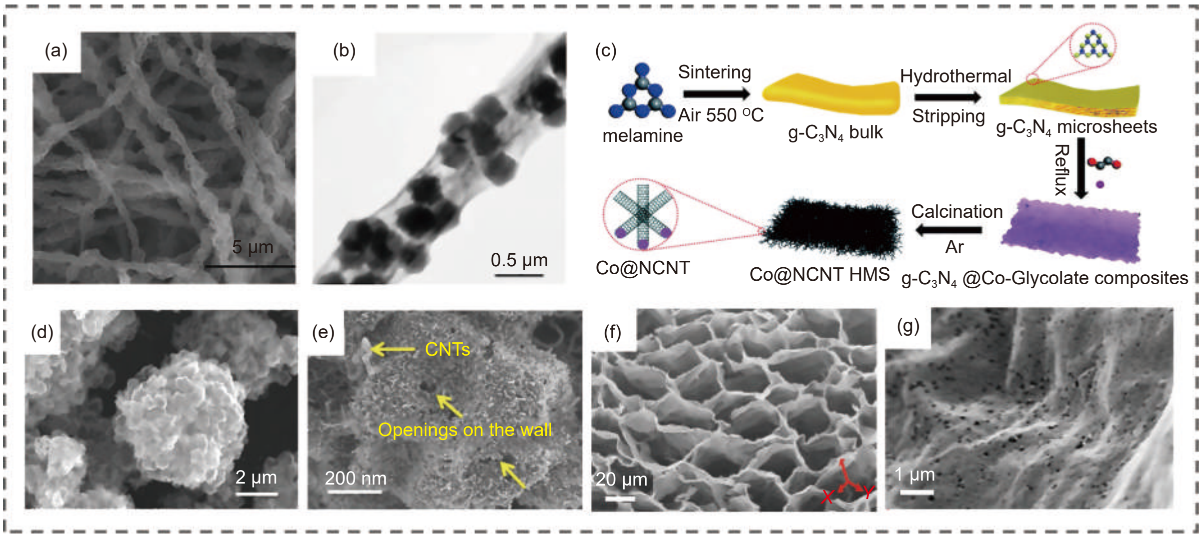

Fig. 6 (a-b) SEM image of Fe-P/NHCF pearl necklace carbon nanofiber[90]. (c) Schematic illustration for the fabrication process of Co @ NCNT HMS[91]. (d-e) SEM images of CoFe$_{20}$@CC[93]. (f-g) SEM images under different magnifications of FeP/Fe$_2$O$_3$@NPCA[94] (Reprinted with permission).

carbon-based catalysts, and considerable efforts have been devoted. The template method usually serves two functionalities. One is to retain the morphology and structure of the precursors, which will prevent the structural collapse during pyrolysis or etching[95–96]. The other is to create porous/hollow structures and provide a high specific surface area, which is beneficial for exposing more active sites[97]. For instance, Feng's group utilized SiO_2 as a hard template to construct a mesoporous carbon nanostructure (SA-Fe-NHPC) (Fig. 7a).

During pyrolysis, the SiO_2 template promoted the generation of hierarchical pores and significantly improved the accessibility of Fe-N_x fraction after subsequent leaching. Utilizing the SA-Fe-NHPC electrocatalyst as the air electrode, the as-assembled ZAB demonstrated a high maximum power density of 266.4 mW cm^{-2} [98]. Xiao et al. successfully developed an advanced self- sacrificing templating method to synthesize graphene sheets dominated by single-atom FeN_4 edge sites by pyrolysis of poly-1,8-diaminonaphthalen, which exhibited great promise as an oxygen electrocatalyst in ZABs. As a result, the Fe/N-G-SAC electrode-based ZAB delivered a narrow charge-discharge gap of 0.78 V as well as negligible losses in activity after 240 cycles[99]. Inorganic salts have excellent thermal stability and can be directly used as templates for carbonization of organic precursors[100,101]. Zhou and co-workers fabricated a 3D porous N-doped graphene (HNG) through pyrolyzing alanine in molten sodium carbonate and post graphitization (Fig. 7b). Due to the combination of catalytically active sites of N-C and the special hierarchical pore structure, the discharge capacity of HNG-based catalysts achieved 790 mAh g^{-1} at 5 mA cm^{-2}, which was much higher than that of Pt/C catalysts[102].

The self-assembly methods to obtain 3D carbon materials have also attracted extensive research interest. Through advanced design of self-assembly methods, carbon materials can be built with different shapes and morphologies, and surface modification[103,104]. For instance, Tang's group synthesized a 3D porous carbon electro-catalyst through growing Co-MOF on graphene with a self-assembly strategy (Fig. 7c). The organic ligands of Co-MOF were immobilized on GO by strong electrostatic attraction, and the electrocatalytic performance of the MOF layers was tuned by precise control of the structure and morphology. Remarkably, the rechargeable ZAB based on as-produced catalyst exhibited a high peak power density of 119 mW cm^{-2} at 0.578 V with a superior stability over 250 charge-discharge cycles (Fig. 7d)[105]. Chen and co-workers synthesized cationic modified colloidal MOFs on negative charged carbon cloth (CC) by an electrodeposition method, which were uniformly distributed on the negatively charged carbon substrates (Fig. 7e). Electrostatic adsorption significantly enriches the feasibilities of constructing

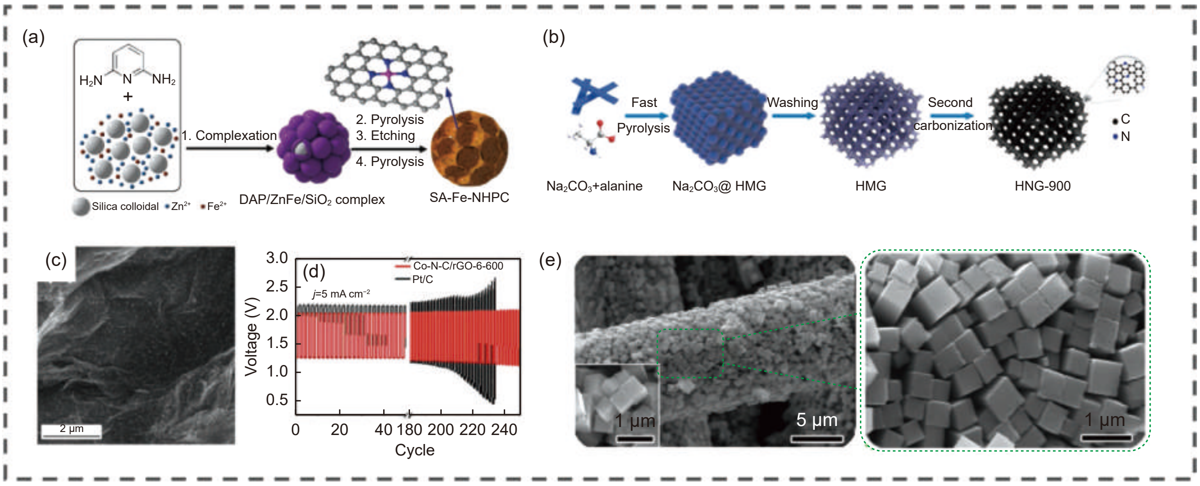

Fig. 7　(a) Schematic illustration of the synthesis of SA-Fe-NHPC[98]. (b) Schematic representation of the fabrication method for 3D HNG[102]. (c) SEM image of Co-N-C/rGO-6-600 catalyst. (d) Cycling performance of rechargeable ZABs based on Co-N-C/rGO-6-600 and commercial Pt/C at 5 mA cm^{-2}[105]. (e) SEM images of the pre-synthesized corresponding colloidal MOFs crystals[106] (Reprinted with permission).

diverse MOFs directly on the substrates. As a result, the ZABs based on the afore-mentioned catalyst displayed an excellent electrochemical stability (up to 400 cycles) and outstanding flexibility[106].

3 Promoting reversibility of Zn anode by multi-dimensional carbon materials

Zn metal anode have been widely studied due to their highly theoretical specific capacity (820 mA hg^{-1}), abundant reserves, low redox potential (−0.76 V vs RHE) and low toxicity[107]. However, issues such as dendrite formation, self-corrosion ($Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2$) and the passivation of Zn anode lead to inferior rechargeability and low Zn utilization (typically < 60% of theoretical capacity), which greatly hinder the large-scale development of ZABs[108–111].

Carbon materials with large specific surface area and low lattice mismatch for Zn deposition to promote the uniform deposition of zinc[112]. For instance, Zhang et al. reported a simple method by pencil drawing zinc anode to restrain dendrite growth and passivation. The functional graphite layer has the advantages of high conductivity and low cost, which can regulate Zn^{2+} uniform deposition behavior. Remarkably, the Zn-G anode exhibits enhanced durability over 200 h and dendrite-free feature (Fig. 8a-b), much better than that of pristine Zn anode (Fig. 8c)[113]. Qian et al. reported a chemical buffer layer consisting of ZnO nanorods and three-dimensional graphene coated on Zn anode (CBL@Zn) to achieve a long-life ZAB (Fig. 8d). The negatively charged CBL is benefit for Zn^{2+} uniform deposition through electrostatic attraction and improved the reversibility of the Zn↔ZnO conversion. Excellent depth of discharge (DOD_{Zn}) up to 98% can be achieved for alkaline ZABs using CBL@Zn electrode, which is much better than bare Zn (Fig. 8e)[114].

Carbon materials with excellent electrical conductivity and large specific area can effectively reduce the local current density of zinc anode to achieve the aims of inhibiting self-corrosion and dendrite growth. In addition, the lightweight of carbon materials can be used as a protective layer for zinc anode and to maximize the energy density of the battery. Thus, carbon materials play an essential role in solving the problems of zinc anode.

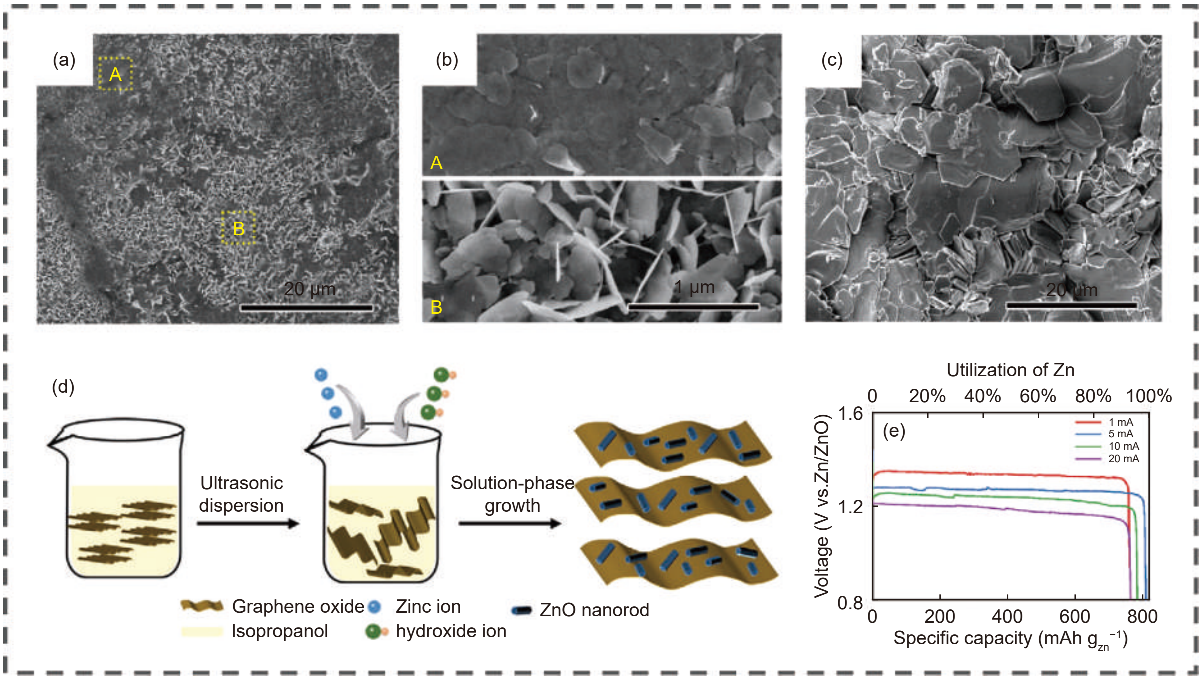

Fig. 8 (a-b) SEM images of Zn-G electrodes . (c) SEM image of Zn after cycling 24 h with the capacity of 1.5 mAh cm^{-2}[113]. (d) Schematic illustration of ZNR@GO image. (e) Chemical buffer layer (CBL) enabled highly reversible Zn anode for deeply discharging and long-life Zn-air battery[114] (Reprinted with permission).

4　Multi-dimensional carbon material-constructed separator

Separator between a cathode and an anode determine the transport of the charged ion species. Generally speaking, the suitable separator of ZABs has the properties with appropriate decomposition[115,116].

Graphene oxide (GO) nanosheets are abundant in functional groups at the base and edges, which can easily be cross-linked to be functionalized with quaternary ammonium (QA) groups. A wide range of polymers can be used as the separator of Zn-air battery. As a typical example, Chen and co-workers firstly prepared a composite membrane with nanocellulose and 2D GO nanosheets. The nanocellulose/GO membrane has the great the hydroxide conductivity and the alkaline stability. As shown in Fig. 9a, the QA-functionalized nanocellulose/2D GO (QAFC GO) membrane was prepared by chemical functionalization, layer-by-layer filtration, cross-linking, and ion-exchange. SEM image shows that the membrane was formed with the functionalized 2D GO nanosheets and cellulose nanofibers alternately (Fig. 9b). The membrane with steady and compact 2D GO protective surface and internal layer has a stable structure, which remains undegraded in water for more than 24 h. In QAFC, the hydroxide ions can transfer between tiguous functionalized sites without any carrier molecules, and the expanded enlarged spacing of GO nanosheets provides more spaces for the hydrated hydroxide ions to migrate (Fig. 9c). In addition, the QAFCGO-based battery exhibited a high open-circuit potential of about 1.4 V[117]. Hereafter, they functionalized GO with 1-hexyl-3-methylimidazolium chloride (HMIM) mo-

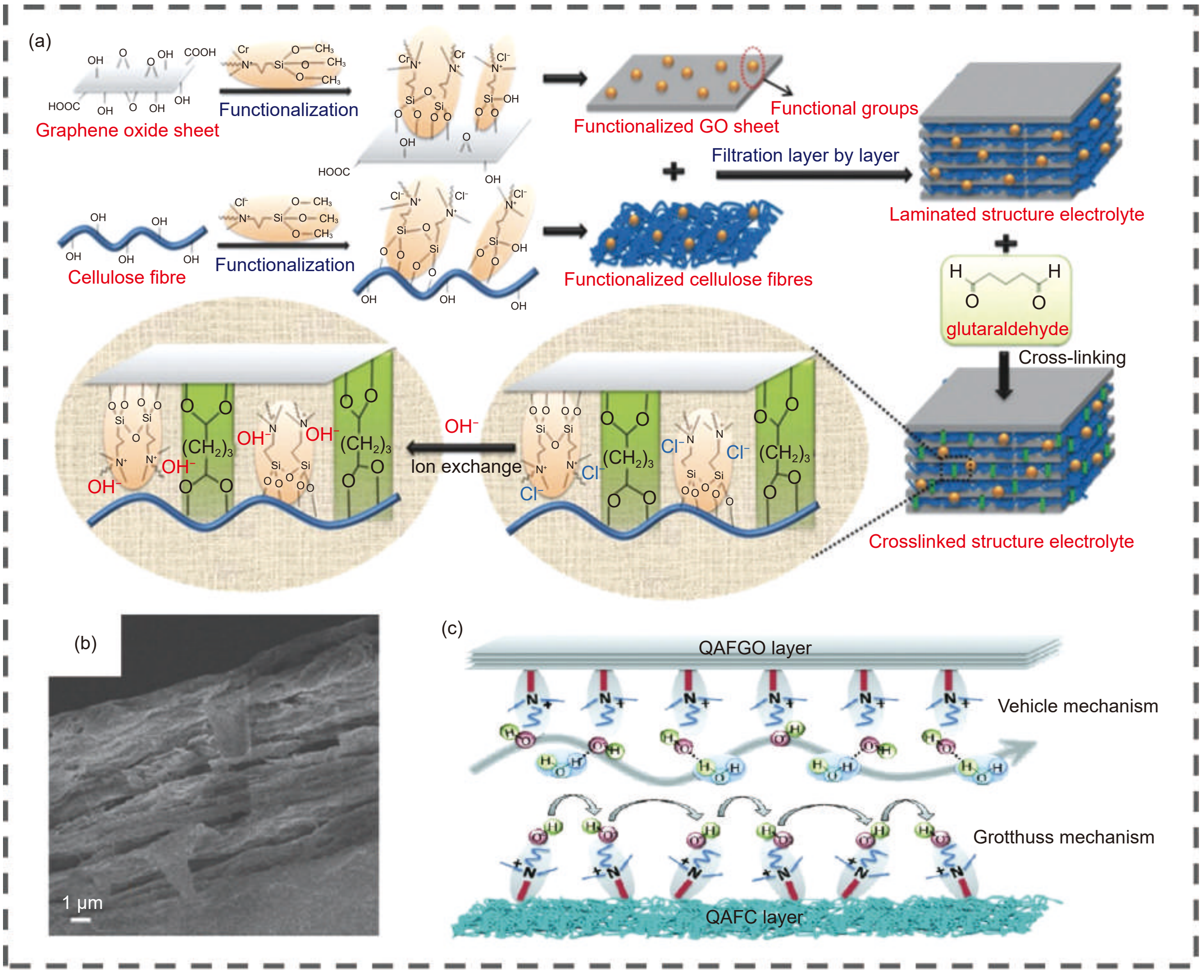

Fig. 9　(a) Schematic diagram of the overall preparation procedure (functionalization, filtration, cross-linking, and hydroxide-exchange) for the QAFCGO membrane. (b) SEM image (cross section) of the QAFCGO membrane. (c) A schematic illustration of ion transport mechanism with QAFGO and QAFC[117] (Reprinted with permission).

lecules. The enlarged spacing between GO nanosheets enhance adsorption of water molecules, which can promote ion transport and remarkably improve the hydroxide conductivity. Therefore, HMIM/GO membrane emerges great hydroxide conductivity and ZAB performance[118].

5 Conclusion

Carbon materials possessing superior electric conductivity, distinct physicochemical properties and favorable electrocatalytic activities have attracted wide attention and provided a great opportunity for the development of ZABs. This review summarizes the recent breakthroughs on the synthesis methods and catalytically active sites of multi-dimensional carbon materials as well as their applications in ZABs. After rational design of multi-dimensional structure, electron transport ability and mechanical strength, carbon materials can be widely applied in each component of ZABs to achieve dramatic battery performance.

Although recent progress strengthened the confidence of researchers towards ZABs, some issues still need solving urgently. First, most of carbon materials with high oxygen-catalytic activities are derived from natural biomass, organic linkers in MOFs, molecules containing carbon element by pyrolysis, which usually suffers from a long preparation cycle, high energy consumption and inferior controllability. Thus, exploring novel methods to achieve environmentally friendliness, synthesis simplicity, high controllability and reproducibility is of great importance. Second, the majority of studies were focused on electrocatalysts of ZABs currently, but Zn anode faces with more serious problems on the enhancement of ZAB performance as it usually has inferior cycling life than air electrodes in alkaline electrolytes. Some research on Zn anode modification based on carbon materials has shown superiority towards the improvement of cycling stability and coulombic efficiency, but the research system mainly was in near-neutral or faintly acid media. More efforts should be performed on Zn anodes to disclose mechanism in alkaline environment. Third, separators in ZABs are usually polyethylene (PE) and polypropylene (PP), which are commonly used in commercial batteries like lithium-ion battery. Therefore, developing a new type of separator with corrosion resistance, suitable pore structure, good ion selectivity and robust mechanical properties to regulate charge distribution on the electrodes and restrain Zn dendritic growth is also a significant research direction in the future. In short, continuing research in this exciting field will facilitate the development of ZABs and their commercialization process.

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