Nanohollow Carbon for Rechargeable Batteries: Ongoing Progresses and Challenges

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HIGHLIGHTS

• The synthesis strategies of nanohollow carbon materials, including nanospheres, nanopolyhedrons, and nanofibers are summarized.
• Nanohollow carbon materials used as electrode materials in several types of rechargeable batteries are reviewed.
• The challenges being faced and perspectives of nanohollow carbon materials are discussed.

ABSTRACT Among the various morphologies of carbon-based materials, hollow carbon nanostructures are of particular interest for energy storage. They have been widely investigated as electrode materials in different types of rechargeable batteries, owing to their high surface areas in association with the high surface-to-volume ratios, controllable pores and pore size distribution, high electrical conductivity, and excellent chemical and mechanical stability, which are beneficial for providing active sites, accelerating electrons/ions transfer, interacting with electrolytes, and giving rise to high specific capacity, rate capability, cycling ability, and overall electrochemical performance. In this overview, we look into the ongoing progresses that are being made with the nanohollow carbon materials, including nanospheres, nanopolyhedrons, and nanofibers, in relation to their applications in the main types of rechargeable batteries. The design and synthesis strategies for them and their electrochemical performance in rechargeable batteries, including lithium-ion batteries, sodium-ion batteries, potassium-ion batteries, and lithium–sulfur batteries are comprehensively reviewed and discussed, together with the challenges being faced and perspectives for them.

KEYWORDS Hollow carbon nanospheres; Nanopolyhedrons and nanofibers; Template synthesis; Rechargeable batteries; Electrochemical performance
1 Introduction

Carbon-based materials are among both the oldest and newest materials, in the entire human civilization of more than 5000 years, and the recent discoveries being fullerenes, carbon nanotubes (CNTs), and more recently graphene [1]. There is no doubt that these carbon-based materials are playing an irreplaceable part in our daily life, the ever-rapidly advancing technologies in the twenty-first century, and future scientific advances. In the past two decades, a series of carbon nanostructures have been developed, such as carbon dots, nanoparticles, nanorods, nanotubes, nanofibers, nanosheets, various core–shells, and nanohollow structures [2–9]. Among them, carbon hollow nanostructures of different morphologies represent a large group of carbon-based materials that have been tuned for high specific surface area in association with the high surface-to-volume ratios, controllable pores and pore size distribution, high electrical conductivity, variable crystallinities, and excellent chemical and mechanical stability [3, 5, 10–12]. By definition, these “nanohollows” refer to the various carbon nanostructures with an appropriate void nanospace distribution inside a distinct nanoshell, either relatively dense or porous, and their dimensions are in the nanometer scales. In morphology, they can be of nanospheres, nanopolyhedrons, and nanofibers.

Since the 1990s, carbon-based materials have been widely employed as electrode materials in various energy storage and conversion devices, especially different types of rechargeable batteries, where graphite is the most widely used anode material for almost all commercial lithium-ion batteries until now [13]. Notably, these rechargeable batteries store charges by the Faraday reaction process and the corresponding electrochemical kinetics are relatively slow [14–16]. For example, carbon materials in any bulk form offer a limited population of active sites and require long ion diffusion pathways, leading to badly compromised reaction kinetics and poor performance. In view of this, carbon-based materials have been largely developed with unique nanostructures to improve the overall electrochemical performance, safety, and durability [17–22]. The development of nanohollow carbon materials (NHCMs) is an effective approach to address some of the bottleneck problems for batteries and other energy storage devices, where their advantages can be listed as follows: Firstly, NHCMs exhibit high surface-to-volume ratios and thus more active sites for charge storages, which would also be beneficial to the shortened electrons transfer/ions diffusion, improved interfacial contact with electrolyte and wettability, resulting in high specific capacity and excellent rate performance. Secondly, NHCMs possess favorable structural and mechanical stability, which can effectively suppress the volume expansion in the repeated long-term cycles of rechargeable batteries, leading to outstanding cycle stability. Thirdly, their morphologies and surface chemistry can be flexibly designed and regulated for different applications. With these appealing advantages, NHCMs have been widely explored as electrode materials in different types of batteries in recent years, which are evidenced by the yearly rising number of scientific publications on nanohollow carbon materials for batteries (Fig. 1).

To design and fabricate NHCMs with different morphologies, various templating and non-templating techniques have been exploited in the past two decades, including silica, polystyrene, calcium carbonate, surfactants, and copolymers for generating emulsion droplets, micelles, vesicles, etc. [2]. Among the various templating techniques, there are both soft and hard templates. For example, one of the early examples of hard templates was the use of hollow silica and inorganic–polymer hybrid nanospheres, reported by Caruso and co-workers in 1998 [23]. In parallel, various chemistry approaches have been taken to manipulate the intrinsic structure, defects, crystallinity, functional groups, and thus the resultant properties, notably by heteroatom (N, B, S, P, etc.) doping of NHCMs, which are aimed at improving the storage capacity and electrochemical kinetics in rechargeable batteries [24–26]. There are several recent reviews on carbon-based materials, such as carbon nanotubes and graphene, for applications in supercapacitors and batteries [27–31]. More

Fig. 1 Number of publications searched by using “hollow carbon materials for batteries” on the Web of Science in the past 10 years
recently, there are also a couple of reviews on carbon nanospheres and core–shell nanostructures for energy storage devices [32–35]. Nevertheless, there is a limited specific discussion in addressing NHCMs, especially with respect to their applications in rechargeable batteries, although there have been a rising number of studies, as mentioned above.

Herein, we will look into the ongoing progresses on the recent development of several key types of NHCMs, including hollow carbon nanospheres, nanopolyhedrons, and nanofibers, and their performances and applications in rechargeable batteries (Fig. 2). Firstly, the design and synthesis strategies of NHCMs through the hard templates, soft templates, and template-free approaches are carefully examined. Given the apparent advantages in structure and electrochemical performance of NHCMs, they have been widely employed as electrode materials for different types of rechargeable batteries, such as lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), potassium-ion batteries (PIBs), and lithium–sulfur batteries (LSBs). There are also the challenges and future perspectives for NHCMs, in particular in connection with the rise of new generation energy storage devices in the coming few years.

2 Controlled Formation of Nanohollow Carbon

Over the past two decades, nanohollow carbon materials (NHCMs) have been considered as an important class of carbon-based materials, and their preparation and performance in energy storage have become a research hot spot. More important than anything else is the controlled formation of nanohollow carbon. In this connection, the use of a pre-made nanostructural template is one of the most effective strategies toward achieving the designed nanohollow structure. Generally, the synthesis strategies for NHCMs can be classified into three major groups, including the hard templates, soft templates, and template-free approach. In parallel, there is a wide range of precursors that have been widely explored for these strategies. Among them, metal–organic frameworks (MOFs) have been studied as both templates and precursors more recently. For nanohollow carbon fibers, electrospinning has been most commonly used.

2.1 Hard Template Methods

Hard templates are among the early approaches to prepare NHCMs, mainly for nanohollow carbon spheres, where the processes generally involve four steps: (1) design of a suitable rigid solid template, (2) coating the template with a carbon precursor, (3) high-temperature pyrolysis, and (4) removing the template. A series of hard templates have been utilized so far, including ceramic types such as silica, polymers such as polystyrene, inorganic salts, and even metallic particles.

Silica (SiO₂) nanospheres are the most widely used hard templates to synthesize NHCMs, owing to their tunable size from nanometers to micrometers, negative surface charge, relatively low cost, as well as good stability. They can be subsequently removed by etching using HF or hot NaOH solution, where the hollow nanostructure can be remained. For instance, Yu et al. designed hollow mesoporous carbon spheres (HMCS) derived from the silica–polydopamine (PDA) nanocomposite spheres by using SiO₂ nanosphere templates [36]. The synthesis diagram of HMCS is shown in Fig. 3a, where the tetraethyl orthosilicate (TEOS) was first added to an EtOH/H₂O/NH₃ mixed solution to form SiO₂ particles (2–3 nm). Notably, the suspension of the
mixed solution could undergo secondary nucleation to form monodispersed SiO₂ clusters. PDA was then added to the reaction system (after the addition of TEOS) for forming a SiO₂@SiO₂/PDA core–shell structure. The HMCS could then be obtained after carbonization and NaOH etching of the SiO₂ templates. The as-synthesized NMCS exhibits a nanohollow spherical structure and controllable pore configuration, cavity size, and shell thickness. In particular, the

Fig. 3  a Schematic illustration of the synthesis process of HMCS by using SiO₂ as hard templates, b–e TEM images of the cavity and shell thickness of the as-fabricated HMCS, scale bars: 100 nm. Reproduced with permission from Ref. [36]. Copyright 2016, Royal Society of Chemistry. f Schematic illustration of the synthesis process of NC, g SEM, and h TEM images of NC. Reproduced with permission from Ref. [40]. Copyright 2017, Elsevier. i, j SEM and k, l TEM images of the carbon colloidosome shells. Reproduced with permission from Ref. [41]. Copyright 2016, Wiley–VCH.
shell thickness of NMCS can be controlled in the range of 15 to 55 nm, and the cavity diameters are in 285–162 nm, respectively (Fig. 3b–e). Noted that there are several carbon source options to achieve the nanohollow carbon spheres, including glucose [37], polypyrrole [38], ionic liquids [39], and so on. These carbon precursors lead to a stable nanohollow structure, when SiO$_2$ is used as a template.

It should be pointed out that the resorcinol–formaldehyde (RF) has been commonly used as a fascinating and versatile carbon precursor. For example, Zhao et al. utilized the RF as the carbon precursor and ethylenediamine (EDA) by a sol–gel method to prepare the N-doped hollow microspheres (NC) (Fig. 3f) [40]. The as-fabricated NC displayed a rather uniform size of ~120 nm with good mechanical strength (Fig. 3g). TEM studies revealed that the NC thus made exhibited hollow nanostructure with a thickness of ~10 nm (shell) and a diameter of ~100 nm (core) (Fig. 3h). Hyeon and co-workers developed nanohollow carbon capsules using phenol resin as the carbon sources and mesoporous SiO$_2$ as the templates [42]. Fuertes et al. produced the SiO$_2$@RF spheres with a core@shell structure [43], where the derived hollow nanostructure is 150–500 nm in diameter. Zheng et al. applied a sol–gel process to synthesize the hollow carbon spheres with a high specific surface area of 1286 m$^2$ g$^{-1}$ [44]. Yu et al. reported a new surfactant-free sequential heterogeneous nucleation pathway using the monodispersed SiO$_2$@RF@SiO$_2$@RF composite to prepare mesostructured nanohollow carbon particles [45].

In addition to the sol–gel processes, SiO$_2$ templates have been employed in other processes as the hard templates, such as chemical self-assembly, chemical vapor deposition (CVD), hydrothermal, and solvothermal approaches. For example, Lou et al. developed a chemically assisted strategy to obtain hollow carbon colloidosomes on various types of functional particles [41]. Their particle sizes can be tuned by size selection of the SiO$_2$ nanosphere templates. As shown in Fig. 3i–l, the as-fabricated hollow carbon colloidosomes exhibit a cavity size of ~400 nm. CVD is an efficient and controllable process to prepare carbon-based materials. Zhao et al. prepared hollow carbon spheres (HCSs) by a CVD method using benzene as the carbon precursor and SiO$_2$ spheres as the templates [46]. The HCSs can be controlled in either smooth single shells, or deformed single shells, or double shells, and N-doped shells. Chen and co-workers also investigated the preparation of hollow carbon materials using the SiO$_2$ template by CVD method [47, 48]. Titirici et al. proposed a hydrothermal carbonization process to achieve hierarchical hollow carbon materials [49], where some functional groups could be anchored on their surfaces under the hydrothermal conditions.

Many other hard templates have been utilized to synthesize nanohollow carbon materials. The surface charges of polystyrene nanospheres (PS) are negative, which is also a class of widely used hard template [50–52]. For instance, Lu and colleagues proposed a confined nanospace pyrolysis process to produce uniform hollow carbon nanospheres (HCNs), by consecutive surface coating on the PS templates [53]. Porous N-doped hollow carbon spheres (PNHCSs) have been prepared using polyaniline as the carbon sources and PS as the templates by Dou et al. [54]. Calcium carbonate (CaCO$_3$) is also an effective hard template for producing NHCMs [55–57]. Our groups developed the N-doped hollow porous carbon spheres (NPCSs) by using CaCO$_3$ spheres as the templates and polydopamine as the carbon source [58]. Notably, the CaCO$_3$ nanosphere can be used as both a hard template and an activator in the high-temperature pyrolysis; thus, the as-prepared NPCS exhibits a high specific surface area of 1984 m$^2$ g$^{-1}$. Besides, some metallic particles have also been proposed as hard templates, such as the metallic Mg [59, 60], Na [61], and Zn [62–64].

### 2.2 Soft Template Methods

Although hard templates have been widely employed in the preparation of NHCMs giving rise to different nanostructures, certain issues exist for them. For example, the hard templates have to be pre-made, which can be a tedious process and add on the overall cost. The processes using hard templates are typically multi-steps and time-consuming, due to the preparation of precursor materials and their coatings, high-temperature carbonization, and the subsequent templates removal by dissolving them in strong acids or alkaline conditions, which are not environmentally friendly. In this regard, soft template methods are more attractive, because the applied templates can either be converted into carbon or be removed in the same carbonization process. Some commonly used soft templates include copolymers and surfactants, which generate the required emulsion droplets, micelles and vesicles, and gas bubbles.
Although various soft templates have been studied and several successful examples have been documented, in general, the successful synthesis of mesoporous or hollow carbon remains a challenge, especially at large scale, due to the relatively weak self-assembly ability of certain precursor components and the likely cross-linking of neighboring building blocks. For example, Qiao et al. used the cationic fluorocarbon surfactant FC4 ($\text{C}_3\text{F}_7\text{O(}\text{CFCF}_3\text{CF}_2\text{O})_2\text{CF CF}_3\text{C ONH(}\text{CH}_2\text{)}_3\text{N}^+\text{(C}_2\text{H}_5\text{)}_2\text{CH}_3\text{I}^-\text{)}$) and triblock copolymer Pluronic F127, $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ (EO, ethylene oxide; PO, propylene oxide) as the soft templates, together with RF as the carbon precursors to prepare mesoporous carbon nanospheres (MCNs) (as shown in Fig. 4a) [65]. By adjusting the key reaction parameters, multi-layered mesoporous RF hollow nanospheres can be synthesized, which can be converted into different hollow MCNs (Fig. 4b–e). Notably, the co-templating of FC4 and Pluronic F127 and the cross-linking properties of the RF precursors, which showed a large degree of shrinkage during the high-temperature pyrolysis process, lead to the formation of hollow or mesoporous carbon nanostructures. Lou et al. proposed the mixed liquids of 1,3,5-trimethylbenzene (TMB) and water with emulsion (a) F127, PPO PEO
Acidic ethanol/water solution Mesoporous polymer nanospheres
Mesoporous carbon nanospheres
Carbonization
TMB amount
Mesoporous spheres TMB droplet Mesoporous Bowl-like particles
Polymerization at the oil/water interface:
Hollow MCMs
Hydrogen-bonding interaction
Surfactant-directed assembly within a droplet-confined space:
In the presence of toluene inside the droplet
In the absence of toluene inside the droplet
In the presence of gas bubbles inside the droplet
Mass ratio of P123 to F127
Multichambered MCMs
Bijel-structured MCMs
Multi-cored MCMs
'Hollow'
MCMs
'Honeycombed' MCMs
In the absence of toluene inside the droplet
In the presence of gas
bubbles inside the droplet
Water
Toluene
Resol
F127
Nanomicelle composite
Aggregation
Bubble
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm
100 nm
Water
Toluene
Resol
F127
Nanomicelle composite
Aggregation
Bubble
100 nm
100 nm
100 nm
100 nm
100 nm
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100 nm

Fig. 4  a Schematic illustration of the formation process of MCNs. b SEM images, c, d TEM images, and e HRTEM image of MCNs. Reproduced with permission from Ref. [65]. Copyright 2013, Nature Publishing Group. f Schematic representation of the mesoporous PDA particle formation. g–i FESEM images of the as-synthesized bowl-like hollow carbon particles. Reproduced with permission from Ref. [66]. Copyright 2016, American Chemical Society. Schematic illustration of j interfacial polymerization of phenolic resol in the presence of Pluronic F127, and k evolution of the interior structures. Reproduced with permission from Ref. [67]. Copyright 2018, Wiley–VCH. l Schematic representation, m FESEM (top), and n TEM (bottom) images of mesophase transition PDA particles with different mass ratios of P123 to F123. Reproduced with permission from Ref. [68]. Copyright 2018, Wiley–VCH. Scale bars are b 1 mm (inset image: 100 nm), c 200 nm, d, g, h 100 nm, e 10 nm, and i 50 nm
droplets as the soft template [66]. The bowl-like hollow PDA particles were synthesized through an emulsion-induced interface anisotropic self-assembly by using the purposely designed TMB soft template and PDA polymer (Fig. 4f). As shown in Fig. 4g–i, the as-derived hollow mesoporous carbon remained a bowl-shaped hollow morphology, with a specific surface area of 619 m² g⁻¹.

Yang et al. also proposed the use of water droplets in nanoparticle-stabilized emulsions (Pickering emulsions) as the soft templates [67]. The interior-structured mesoporous carbon microspheres (MCMs) could be successfully obtained by the surfactant assembly within the pickering emulsion droplets templates, and the phenolic resole oligomers were used as the carbon precursors. In particular, the phenolic resole oligomers were co-assembled with Pluronic F127 molecules via hydrogen bonding interactions, and the formation of the nanomicelle-type composite induced a new oil/water interface, leading to a mesoporous structure at around the inner surface of the water droplet (Fig. 4j). The interior structures of MCMs thus derived (such as hollow, multi-chambered, bijel-structured multi-cored “solid,” and honeycombed) could be regulated by tailoring the concentration of nanomicelles with water droplets (Fig. 4k). Similarly, Ji et al. produced N-doped hollow nanospheres (N-NHCM) through the carbonization of hollow ZIF-8 nanospheres, which were prepared by an emulsion-based interfacial reaction [69]. In addition, Yao and co-workers presented an approach of using o-phenylenediamine (oPD) oligomers as the soft templates, by hydrogen bonding to form polymer microspheres [70], which could be transformed into nitrogen and oxygen co-doped hollow carbon spheres (HCSs) upon high-temperature pyrolysis process. Subsequently, Ye et al. applied an O/W/O inverse-emulsion system as the soft template and RF as the carbon precursor to develop hollow carbon particles [71].

While the soft templates can lead to mesoporous hollow materials, a precision regulation in the pore configuration and feature remains a challenge in several studied systems. In this regard, Lou et al. proposed a novel dual-soft-template approach to prepare walnut-shaped macro/mesoporous PDA particles with bicontinuous channels ranging from 20 to 95 nm [68]. A mixture of two similar block copolymers (P123 and F127) was employed as the dual soft templates in their research. Note that the mass ratio of P123 to F127 has a great impact on the mesophase transition for the formation of mesostructured PDA particles (Fig. 4). As shown in Fig. 4m, n, the walnut-shaped PDA particles could be carbonized into hollow mesoporous carbon particles with morphology and pore structure largely unchanged. Besides, some common surfactants could also be used as the soft templates to prepare nanohollow carbon materials [72]. For instance, Li and Zhang et al. utilized the anionic surfactant sodium dodecyl sulfate (SDS) as the soft template to synthesize hollow carbonaceous capsules and hollow carbon nanospheres, respectively [73, 74]. Tashima and co-workers proposed the cetyltrimethylammonium bromide (CTAB) as the soft template and 1,3,5-trimethylbenzene (TMB) and tertbutanol (t-BuOH) as the co-surfactants to prepare nanohollow carbon materials [75, 76].

2.3 Template-Free Methods

Although both the hard template and soft template methods have been widely employed in the synthesis of nanohollow carbon materials up to now, the hard template strategies are typically multi-steps and time-consuming owing to the need for preparation and subsequent removal of precursor template materials. It is also difficult to accurately tune the hollow morphologies and components of NHCMs by using the soft template strategies. To this end, the template-free approach is a facile and low cost for synthesizing NHCMs.

In this connection, certain hollow polymers/precursors can be prepared by self-polymerization or self-assembling, and then, a high-temperature pyrolysis is carried out to overt them into NHCMs. For example, Wu and co-workers synthesized the amphiphilic homopolymer (PAA) through a polymerization process without any templates, which could be self-assembled into rather uniform vesicles by directly adding water to the PAA solution without any purification (Fig. 5a) [77]. As shown in Fig. 5b, c, the diameter of the as-assembled PPA vesicles was ~200 nm. By the electron transmittance chart and electron transmittance simulation, the membrane thickness of PAA vesicles was ~5 nm (Fig. 5d, e). Nitrogen-doped hollow carbon spheres (N-HCSs) can then be prepared by the carbonization of the PAA vesicles cross-linked by melamine. Authors group also developed a controllable solvothermal route to design the N-doped hollow carbon microspheres (N-HCMs), which were formed by the self-assembly of hierarchical polyimide nanosheets by controlling of a suitable polymerization time and solvent without any additional catalyst and template [78]. The as-fabricated NHCM displayed a
hierarchical porous structure with a high specific area of 1005 m² g⁻¹. Notably, the template-free method for fabricating NHCM is environment friendly and does not require the tedious processes of adding and removing any templates. For example, Wu and Niwase et al. prepared hollow carbon materials through heat treatment of the resole modified with poly(ethylene glycol) monomethyl ether (resole-PEG), with C60 fullerene powder as the polymeric carbon precursor [79, 80]. Hui et al. utilized the solid melamine–formaldehyde resin spheres to develop nitrogen- and oxygen-co-doped hollow carbon spheres (HCSs) by high-temperature pyrolysis [81].

Self-assembly provides a promising pathway for the synthesis of carbon-based materials with nanohollow structures. Long et al. reported hollow polyacrylonitrile (PAN) spheres by a gas-foaming-assisted phase-inversion process, where the liquid–liquid phase-inversion process and a self-assembly process were coupled (Fig. 5f) [82]. As shown in Fig. 5g, the PAN spheres thus made showed robust and hollow architectures, and their sizes could be tailored by changing the needle sizes and the temperatures of the water bath. The mechanical properties of the hollow composite-type spheres could be enhanced through adding CNTs in the precursor solution (Fig. 5h). Hollow carbon spheres (HCSs) were then obtained by the carbonization of the oxidized PAN spheres by a high-temperature treatment. Similarly, spray pyrolysis has been considered as an effective to prepare nanohollow carbon materials [84, 85]. For instance, S. Suslick et al.
proposed an ultrasonic spray pyrolysis to synthesize porous carbon materials with alkali propiolates (HC≡CCO₂M, M = Li, Na, and K) as the carbon precursors [83]. As shown in Fig. 5i–k, different structures and morphologies of hollow carbon materials can be formed by mixing the alkali propiolates with different mole ratios. A one-step aerosol process to synthesize hollow carbon nanoparticles has been reported by Lu and co-workers, who employed an enzymatically polymerized poly(4-ethylphenol) as the carbon precursor [86]. NHCMs can be also formed through a proper plasma process. For example, Kim and Charlier et al. proposed an electric plasma discharge and thermal plasma process to prepare hollow carbon materials [87, 88]. García and co-workers presented a study on the chlorination of bis(benzene)chromium (Cr(C₆H₆)₂) to achieve the hollow and solid carbon spheres at two reaction temperatures [89]. The as-fabricated hollow carbon spheres exhibited a high surface area of 1761 m² g⁻¹.

2.4 MOFs-Derived Hollow Carbon Nanopolyhedrons

Metal–organic frameworks (MOFs) are crystalline coordination compounds composed of metal ions (or metal clusters) and organic ligands, which have attracted much attention both scientifically and technologically [90]. Due to their tunable chemical compositions, morphologies, level of porosity, international pore configuration, and surface functionalities that can be regulated by the combinations of organic and metal/inorganic constituents, they have been widely applied in adsorption, gas storage, catalysis, drug delivery, energy storage, and conversion [91]. In addition, MOFs have been demonstrated as excellent precursors to prepare various porous materials, including those carbon-based, as reported by Xu and co-workers in 2008 [92]. A subsequent report on MOFs-derived porous carbon was made by Yamauchi et al. in 2012 [93]. Since then, MOFs-derived carbons have emerged as a large class of porous materials studied for various applications [3, 94, 95]. Nevertheless, the common challenges for these MOFs-derived carbon materials are related to the carbonization process, such as the undesired pore structure formed, aggregation of metal/nonmetal particles, and poor control in structural evolution [20]. To address some of these issues MOFs themselves can act certain templating roles, in addition to being the precursors. Therefore, considerable efforts have been made in the tuning of various processing conditions to form the designed MOFs in the first place, and then the condition to convert them into the desired hollow/porous carbon-based structures. Similarly, there has been considerable progress made with both the hard and soft templating of MOFs and MOF-derived carbon-based materials. In this connection, some of the governing principles that have been discussed above on the hard and soft templating approaches would be applicable to them.

As a main elemental component in MOFs is carbon, carbon-based materials can be derived by carbonization of MOFs without adding other precursors. However, due to the rather complicated steps involved in the actual conversion process, there is need to control the processing conditions applied to the carbonization process, such as temperature, atmosphere/medium, and even time. In the process, there are steady changes in the chemical composition, types of phases, both internal pore structure and surface conditions, as well as morphology. A few MOFs can be converted into hollow carbon structure, by carefully choosing the MOF types and experimental conditions. To tailor the desired hollow carbon structure, certain templating approach is shown to be useful. For example, in a stress-induced orientation contraction approach, Ye and co-workers used ZIF-8 nanotubes as the precursor and then coated them with a thick and thin mesoporous silica layer (mSiO₂), respectively. Mesoporous hollow carbon nanotubes (HMCNCs) and solid mesoporous carbon nanotubes (SMCNCs) without hollow cavity could then be obtained after pyrolysis and acid treatment (Fig. 6a, b) [96]. The ZIF-8 nanotubes would have contracted strongly during the high-temperature pyrolysis process, and the carbonization occurred preferentially at the interface between ZIF-8 and mSiO₂ coating, where the thick mSiO₂ layer was rigid enough to counteract the inward contraction, but not the thin mSiO₂ layer, so the respective HMCNCs and SMCNCs were formed by the different mSiO₂ thicknesses. The SEM and TEM images of the HMCNCs (the thickness of mSiO₂ was about 40 nm, Fig. 6c–e) and SMCNCs (the thickness of mSiO₂ was about 8 nm, Fig. 6f–h) further explain that the rigid-interface-induced outward contraction by the mSiO₂ layer thickness was effective to regulate ZIF-8 derived carbon structure. Besides, the mesoporous silica (mSiO₂) had been coated on the Co-based MOFs (ZIF-67) to synthesize 3D hollow carbon materials, together with carbon nanotubes on their surface by the Co catalysis during the pyrolysis process [97]. Similarly, carbon nanotube-decorated N-doped hollow carbon can be prepared through pyrolysis...
of SiO$_2$ and bimetallic ZIFs-Co$_x$Zn$_{1-x}$ based on a mixed ions strategy [98]. Hollow N-doped carbon can be also achieved using ZIF-8 as the cores and polydopamine (PDA) as the shells via heat treatment by the stresses-induced orientation contraction [99].

The synthesis of MOFs-derived hollow carbon nanopolyhedrons has been successfully demonstrated through SiO$_2$ coating, carbonization, and etching process, whereas this procedure requires a uniform coating around the high-curvature surface and post-treatment to remove the template, which is rather complicated and time-consuming. Yamauchi and co-workers had proposed that ZIF-8 could be used to fabricate hollow carbonaceous composites through a hydrothermal reaction with glucose (Fig. 6i), where the acid generated from the hydrolysis of glucose led to the decomposition of ZIF-8 [100]. As shown in Fig. 6j, k, ZIF-8-derived hollow carbonaceous composites can be transformed into hollow carbon and ZnO/C nanocomposites after pyrolysis at 900 and 500 °C, respectively. They have also developed a spatially controlled tannic acid solution etching strategy to prepare monocrystalline ZIF nanobubbles (Fig. 6l), which can be converted into hollow carbon nanobubbles under an optimal pyrolytic condition [101]. Furthermore, Wang et al. found that the phytic acid (PA) can slowly etch ZIF-67, forming a hollow nanostructure [102]. More recently, a series of MOFs-derived hollow carbon nanopolyhedrons have been

Fig. 6 Schematic illustration of the fabrication processes of a HMCNCs and b SMCNCs. c, f SEM images, d, g TEM images, and e, h electron tomography slices of carbon@mSiO$_2$-40 and carbon@mSiO$_2$-8, respectively, scale bar: 100 nm. Reproduced with permission from Ref. [96]. Copyright 2018, Wiley–VCH. i Schematic illustration of the preparation of hollow carbonaceous materials. j SEM, and k TEM images of the HZC-2.5 M-2 h. Reproduced with permission from Ref. [100]. Copyright 2018, American Chemical Society. l Schematic illustration of the spatially controlled etching to produce monocrystalline ZIF nanobubbles. Reproduced with permission from Ref. [101]. Copyright 2017, Royal Society of Chemistry
reported by using MOFs as the cores (structural templates) and various polymers as the shells achieved through high-temperature pyrolysis [103]. The polymer coating layers, such as poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS) [104, 105], oligo(cyclotriphosphazene-co-hexahydroxytriphenylene) (OCHT) [106], and resorcinol–formaldehyde polymers [107], have been demonstrated to be feasible.

2.5 Electrospinning of Hollow Carbon Nanofibers

One-dimensional (1D) hollow carbon nanofibers have been exploited for energy storage and conversion, owing to their large length to diameter ratio and high surface area, which can provide charge storage sites and fast pathways for electron transport [3]. These 1D hollow carbon nanofibers also show robust mechanical flexibility, which can be easily grown on to substrate supports to form self-standing flexible electrodes for energy storage devices. Up to now, there are several strategies to prepare the 1D carbon nanofibers, such as electrospinning, template synthesis, chemical vapor deposition, hydrothermal growth, and self-assembly. Among them, electrospinning is considered as the most facile and highly controllable approach to achieve the designed carbon nanofibers with hollow nanoarchitectures and freestanding functionality, including those uniaxial, co-axial, and triple-co-axial ones.

Due to the high carbon yield and predictable mechanical strength of the resultant products, polyacrylonitrile (PAN) has been widely employed as the carbon precursor for electrosynthesis of carbon nanofibers, where co-axial electrospinning is the commonly used method for manufacturing 1D hollow carbon nanofibers. For example, Shanmugam and co-workers prepared hollow (HCNR)- and arch (ACNR)-shaped carbon nanotubes by the co-axial electrospinning (Fig. 7a), where PAN was used as the carbon precursor and polyvinyl pyrrolidone (PVP) was used as the sacrificial polymer with different flow rates [108]. As shown in Fig. 7b–e, the as-fabricated HCNR and ACNR nanostructures showed average diameters of 180 and 155 nm, where the core diameter was about 40–70 nm for the HCNR sample. Similarly, N-doped hollow carbon nanofibers (HACNFs) have been prepared via the co-axial electrospinning using PVP as the core precursor and PAN as the shell precursor, together with NH3 activation treatment (Fig. 7f) [109]. The as-obtained HACNFs exhibited an outer and an inner fiber diameter of ~300 and ~150 nm, as well as a high specific surface area of 655 m2 g−1. Up to now, different internal and external polymer precursor components have been developed for preparing hollow carbon nanofibers by the co-axial electrospinning, including a mixture of PAN/PVP as the shell and PV as the core precursor [110], poly(styrene-co-acrylonitrile) (SAN) as the core and PAN/PVP mixture as the shell precursor [111], SAN solution as the core and polyacrylic acid (PAA) as the shell precursor [112], poly (methyl methacrylate) (PMMA) as the core precursor and PAN/PMMA mixture as the outer shell precursor [113], silicone oil as the inner core and PAN as the outside layer precursor [114], and so on [115, 116].

1D hollow carbon nanofibers can also be prepared by uniaxial electrospinning technique, which needs some additional materials to assist the synthesis. For instance, the hollow particle-based N-doped carbon nanofibers (HPCNFs-N) have been prepared by the carbonization of PAN/ZIF-8 composite nanofibers (Fig. 7g), where the ultrafine ZIF-8 nanoparticles were embedded into electrosynthesized PAN precursor [117]. The primary ZIF-8 nanoparticles could be transformed into interconnected N-doped carbon hollow nanoparticles by high-temperature carbonization. As shown in Fig. 7h–k, the as-fabricated HPCNFs-N exhibited good flexibility, which consisted of numerous hollow nanoparticles interconnected with each other. Owing to such hierarchical porous structure (417.9 m2 g−1) and high N-doping level (7.85%), the HPCNFs-N showed remarkable specific capacitances and excellent cycle stability, when used as electrodes in supercapacitors. Similarly, Wang et al. also reported the preparation of N-doped hollow hierarchical carbon fibers (NCFs) via electrospinning and further carbonization of the ZIF-8/PAN nanofibers [118]. The hard/soft templates materials were added to the electrospinning polymer solution for achieving the hollow carbon nanofibers. For example, Cui and co-workers used SiO2 as the template and pore-forming agent to prepare hollow bamboo-like carbon nanofibers [119]. Other hard templates included ZnO [120], SnO2/Fe2O3 [121], and PS microspheres [122]. Several soft templates have been also proposed to obtain hollow carbon nanofibers [123], together with triple-co-axial electrospinning, nozzle-less electrospinning, and other approaches [124–126].

3 Application in Rechargeable Batteries

Lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), potassium-ion batteries (PIBs), and lithium–sulfur batteries (LSBs) are among the rechargeable batteries. The electrochemical performances of these battery systems
are largely determined by the electrode materials, and thus, the development of a superior electrode material plays an important role in these rechargeable batteries. Indeed, nanohollow carbon materials (NHCMs) have been widely investigated as the electrode materials; in particular, those hollow carbon nanospheres exhibit high surface-to-volume ratios, encapsulation capability, together with outstanding electrochemical performance when used in batteries, especially using as conductive host materials offer to inhibit the polysulfide entrapping and buffer the volume expansion in lithium–sulfur batteries. However, owing to nanohollow carbon spheres having the lower tap density and the larger cavity volume than some of hollow carbon materials, they give rise to a relatively lower

![Diagram](image-url)
volume energy density in the as-assembled batteries. In addition, the structural stability of hollow carbon nanoparticles needs to be further improved during the repeated cycles. MOF-derived carbon nanopolyhedrons possess high specific surface areas and tailorable levels of porosity, which would aid to provide a path way for electrons to move and shorten the length of transfer channel. Nevertheless, the production yield of MOF-derived carbon nanopolyhedrons is low; this is a torturous problem for large-scale application in batteries. Hollow carbon nanofibers afford a high surface-to-volume ratio and a short transport pathway for ions, and they also show favorable opportunities in flexible battery devices, owing to their unique 1D morphology and outstanding flexibility. Even so, the reactive sites exposed by nanohollow carbon nanofibers are relatively limited, and thus, a combination of multiple activation strategies has often been employed when used in batteries. Even so, the reactive sites exposed by the nanohollow carbon nanofibers are relatively limited in number. Thus, an efficient combination of multiple entities would be of value for applications in batteries. For example, rechargeable batteries making use of a combination of different types of nanohollow carbons as the electrode materials can give rise to a high specific capacity, rate capability, and cycle stability. Some of the application examples are listed in Table 1, where they are compared with those with graphite and conventional carbon materials.

3.1 Lithium-Ion Batteries

Lithium-ion batteries (LIBs) have been dominating the power market for portable electronics, and now they are quickly moving into hybrid vehicles and electric transport systems. Graphite anode has been widely used in commercial LIBs, owing to the large specific capacity (372 mAh g\(^{-1}\)), mechanical robustness, and long cycle stability. However, its poor Li\(^+\) diffusion kinetics and thick solid electrolyte interphase (SEI) often lead to an inferior rate capability. Up to now, there have been a large number of studies on using nanohollow carbon as the electrode materials for LIBs. For instance, Goodenough and co-workers proposed an in situ chemical deposition strategy to grow CNT on the surface of the N-doped CNFs, where C\(_2\)H\(_2\) as the carbon source and Ni particles as the catalyst, yielding an activated N-doped hollow CNT–CNF hybrid materials (Fig. 8a) [127], in which Ni nanoparticles were encapsulated in graphicitc carbon with a thickness of ~5 nm (Fig. 8b). They possessed pores and hollow carbon nanoparticles, and defects were present in the wall of hollow structure (Fig. 8c, d). As shown in Fig. 8e, such material gave a reversible capacity of about 1150 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\). At the high current density of 8 A g\(^{-1}\), its capacity of ~320 mAh g\(^{-1}\) fades less than 20% after 3500 cycles. There are a number of reports on the synthesis of nanohollow carbon materials by template method used for LIBs [128–132, 177, 178]. For example, N-doped mesoporous carbon hollow spheres (N-MCHSs) were synthesized by using mesoporous silica hollow spheres as the template and PDA as carbon precursor, reported by Chu et al. [133]. They displayed a sponge-like mesoporous shell and showed a high specific surface area of 411.6 m\(^2\) g\(^{-1}\). Yu et al. reported graphene-wrapped graphitic hollow carbon spheres (G-graphitic HCS), which were fabricated by iron-catalyzed carbonization of double-coated PS spheres template [134]. They delivered a high initial discharge capacity of 2007 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and remained 92.4% of initial capacity after 100 cycles.

As has been mentioned above, electrospinning is an effective strategy to prepare hollow carbon fibers, which have been applied to LIBs [124, 179, 180]. Chen et al. synthesized a self-healing core fiber with the liquid metal nanoparticles, which were encapsulated with hollow carbon (LMNPs@CS) by the co-axial electrospinning and then carbonization (Figure 8f) [135]. The LMNPs@CS fiber was used as a freestanding anode and showed an impressive rate capability (499 mAh g\(^{-1}\) at 2 A g\(^{-1}\)) and excellent cycle stability (552 mAh g\(^{-1}\) after 1500 cycles) (Fig. 8g). Yu et al. also proposed a co-axial electrospinning pathway to make hollow carbon nanofibers (HCNFs) as anode materials for LIBs, where the styrene-co-acrylonitrile is the core and poly(acrylonitrile) is the shell solutions, together with a subsequent thermal treatment process [137]. Recently, Lee and co-workers presented a method involving urea coating over the electrospun PAN fibers before the carbonization process [138]. The obtained hollow carbon nanofibers exhibit a significant change in porous structure, which demonstrates a high specific capacity of 520 mAh g\(^{-1}\) at 1 C current density when used as the anode for LIBs. Li and co-workers presented a freezing-assisted strategy to achieve N and O co-doped hollow carbon spheres (DHCSs/RGO) composite material (Fig. 8h) [136]. They were coated with
Table 1 Overall electrochemical performances of rechargeable batteries making use of nanohollow carbons, graphite, and hard carbon materials

| Batteries | Materials                                      | Highest capacity (mAh g⁻¹) | Rate capability (mAh g⁻¹) | Cycle numbers | References |
|-----------|-----------------------------------------------|-----------------------------|----------------------------|---------------|------------|
| LIBs      | N-doped hollow CNT–CNF                        | 1150 at 0.1 A g⁻¹           | 320 at 8 A g⁻¹             | 3500          | [127]      |
| LIBs      | N-doped hollow carbon nanoflowers             | 528 at 2 C                  | 298 at 10 C                | 1000          | [128]      |
| LIBs      | N-doped double-shelled hollow carbon spheres  | 920.3 at 0.1 A g⁻¹          | 292.9 at 5 A g⁻¹           | 300           | [129]      |
| LIBs      | Macro–mesoporous hollow carbon spheres        | 530 at 2.5 A g⁻¹            | 180 at 60 A g⁻¹            | 1000          | [130]      |
| LIBs      | Carbohydrate-derived hollow carbon spheres    | ~400 at 1 C                 | ~100 at 2 C                | 200           | [131]      |
| LIBs      | Hollow carbon nanoparticles                    | 863 at 0.1 A g⁻¹            | 171 at 6.4 A g⁻¹           | 200           | [132]      |
| LIBs      | N-doped mesoporous carbon hollow spheres      | 485 at 0.5 A g⁻¹            | 214 at 4 A g⁻¹             | 1100          | [133]      |
| LIBs      | Graphitic hollow carbon spheres               | 2007 at 0.1 A g⁻¹           | 410 at 5 A g⁻¹             | 1000          | [134]      |
| LIBs      | Self-healing core–shell hollow carbon fibers  | 603.9 at 1 A g⁻¹            | 499 at 2 A g⁻¹             | 1500          | [135]      |
| LIBs      | N and O co-doped hollow carbon spheres        | 1395 at 0.1 A g⁻¹           | 606 at 5 A g⁻¹             | 600           | [136]      |
| LIBs      | Hollow carbon nanotubes                       | 517.7 at 0.05 A g⁻¹         | 436.4 at 0.2 A g⁻¹         | 2000          | [137]      |
| LIBs      | N-doped hollow carbon fibers                  | ~600 at 0.5 C               | ~200 at 50 C               | 500           | [138]      |
| LIBs      | Graphite                                      | 393 at 0.1 C                | ~120 at 10 C               | 800           | [139]      |
| LIBs      | Holey graphite                                | 425.7 at 0.1 C              | 95.7 at 2 C                | 500           | [140]      |
| LIBs      | Natural graphite                              | 395.6 at 0.1 C              | 246 at 50 C                | 200           | [141]      |
| SIBs      | Multi-shelled hollow hard carbon nanospheres  | 360 at 0.03 A g⁻¹           | 200 at 0.6 A g⁻¹           | 150           | [142]      |
| SIBs      | Hollow carbon nanospheres                     | 160 at 0.2 A g⁻¹            | ~50 at 10 A g⁻¹            | 100           | [143]      |
| SIBs      | P-doped hollow carbon sphere                  | 234 at 0.1 A g⁻¹            | 129 at 1.5 A g⁻¹           | 300           | [144]      |
| SIBs      | S/N-co-doped hollow carbon spheres            | 185 at 0.5 A g⁻¹            | 110 at 10 A g⁻¹            | 2000          | [145]      |
| SIBs      | N-containing hollow carbon microspheres       | 296 at 0.2 A g⁻¹            | 114 at 10 A g⁻¹            | 1200          | [146]      |
| SIBs      | Hollow carbon nanowires                       | 251 at 0.05 A g⁻¹           | 149 at 0.5A g⁻¹            | 500           | [147]      |
| SIBs      | Hollow carbon nanofibers                      | 326 at 0.02 A g⁻¹           | 85 at 1.6 A g⁻¹            | 5000          | [148]      |
| SIBs      | N/P co-doped hollow carbon nanofibers         | 358 at 0.05 A g⁻¹           | 140 at 5 A g⁻¹             | 2000          | [149]      |
| SIBs      | N/S dual-doped hollow carbon fibers           | 264 at 0.1 A g⁻¹            | 64 at 10 A g⁻¹             | 4000          | [150]      |
| SIBs      | Polyhedral-shaped hollow porous carbon        | 227 at 1 A g⁻¹              | 133 at 20 A g⁻¹            | 9000          | [151]      |
| SIBs      | 3D hollow reticulate hard carbon              | 160 at 0.05 A g⁻¹           | 50 at 2 A g⁻¹              | 1000          | [152]      |
| SIBs      | Hard carbon                                   | 430.5 at 0.03 A g⁻¹         | ~50 at 2 A g⁻¹             | 200           | [153]      |
| SIBs      | Orange peel-derived hard carbon               | 180 at 0.015 A g⁻¹          | ~120 at 0.14 A g⁻¹         | 100           | [154]      |
| SIBs      | Defective hard carbon                         | ~300 at 0.1 A g⁻¹           | ~125 at 2 A g⁻¹            | 200           | [155]      |
| PIBs      | Sulfur-grafted hollow carbon spheres          | 581 at 0.025 A g⁻¹          | 110 at 5 A g⁻¹             | 1000          | [156]      |
| PIBs      | Activated hollow carbon nanospheres           | 370.2 at 0.2 A g⁻¹          | 137 at 4 A g⁻¹             | 5000          | [157]      |
| PIBs      | N-doped hollow carbon nanospheres             | 326 at 0.05 A g⁻¹           | 141 at 2 A g⁻¹             | 2500          | [158]      |
| PIBs      | Hollow interconnected neuron-like carbon      | 340 at 0.1 C                | ~100 at 2 C                | 500           | [159]      |
| PIBs      | Hollow multihole carbon bowls                 | 304 at 0.1 A g⁻¹            | 182 at 2 A g⁻¹             | 1000          | [160]      |
| PIBs      | Soft carbon semi-hollow microrods             | 314 at 0.1 A g⁻¹            | ~100 at 1 A g⁻¹            | 500           | [161]      |
| PIBs      | Graphite                                      | 263 at 0.1 C                | 80 at 1 C                  | 50            | [162]      |
| PIBs      | Graphite                                      | ~232 at 0.5 C               | /                          | 50            | [163]      |
| PIBs      | Graphite                                      | ~200 at 0.5 C               | ~80 at 2 C                 | 700           | [164]      |
| LSBs      | Hollow nitrogen-doped carbon nanospheres      | 1286 at 0.1 C               | 623 at 5 C                 | 800           | [165]      |
| LSBs      | Fructose-derived hollow carbon nanospheres   | 1043 at 0.1 C               | 483 at 5 C                 | 200           | [166]      |
| LSBs      | N-doped porous hollow carbon nanosphere       | 1224 at 0.2 C               | 720 at 5 C                 | 500           | [167]      |
| LSBs      | Hollow N-doped carbon polyhedrons            | 737.1 at 0.2 C              | 501.3 at 1 C               | 500           | [168]      |
| LSBs      | Hollow carbon nanofibers                      | 1180 at 0.2 C               | 820 at 1 C                 | 300           | [169]      |
| LSBs      | Hollow carbon nanofibers                      | 1170 at 1 C                 | 860 at 4 C                 | 300           | [170]      |
| LSBs      | Hollow carbon nanofiber arrays                | 730 at 0.2 C                | /                          | 150           | [171]      |
| LSBs      | N-doped hollow carbon spheres                 | 1249 at 0.1 C               | 688.4 at 2 C               | 50            | [172]      |
| LSBs      | 3D hyperbranched hollow carbon nanorod        | 1378 at 0.1 C               | 663 at 10 C                | 500           | [173]      |
thin RGO nanosheets to form a homogeneous 3D porous network architecture. Owing to the hierarchical porous structure and high-level of heteroatom doping, the DHCSs/RGO electrode showed excellent electrochemical performance for LIBs, including a high reversible capacity (1395 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\)), outstanding rate capability (606 mAh g\(^{-1}\) at 5 A...
and long cycle life (600 cycles). Other strategies, such as directly carbonized [181–183], self-assembled [184–186], and microwave-assisted [187], have been employed to prepare nanohollow carbon materials for application in LIBs.

3.2 Sodium-Ion Batteries

As a low cost and sustainable alternative to LIBs, sodium-ion batteries (SIBs) have been extensively studied over the past few years. The radius of Na⁺ is much larger than that of Li⁺ (1.5 times), often leading to slow intercalation kinetics and poor performances. As an electrode material, hollow carbon nanostructure can provide more space for Na⁺ intercalation and low energy barrier, thus improving the electrochemical kinetics and overall performances. For example, Wan and co-workers proposed a controllable structure engineering to prepare multi-shelled hollow hard carbon nanospheres (MS-NHCMs), which were derived from the hollow resin nanospheres with 3-aminophenol (3-AP) and formaldehyde (3-AF) as the precursors (Fig. 9a) [142]. In particular, single-shelled NHCM (1S-NHCM), double-shelled NHCM (2S-NHCM), three-shelled NHCM (3S-NHCM), and even four-shelled NHCM (4S-NHCM) could be realized through accurate control of the shape parameters (Fig. 9b–e). These NHCM electrodes can deliver better electrochemical performance compared with other carbon-based materials for SIBs. For example, the 4S-NHCM showed a high specific capacity of 360 mAh g⁻¹, good rate capability (200 mAh g⁻¹ at 2 C), and cycle stability for 150 cycles (Fig. 9f). There are other studies on hollow carbon microspheres, reported for

Fig. 9  a Schematic illustration of the synthesis process for MS-NHCM. SEM and TEM images of b 1S-NHCM, c 2S-NHCM, d 3S-NHCM, and e 4S-NHCM samples.  f Electrochemical performances of all NHCM electrodes for SIBs. Reproduced with permission from Ref. [142].  Copyright 2018, Wiley–VCH.  g, h SEM images of HCNWs. Reproduced with permission from Ref. [147].  Copyright 2012, American Chemical Society.  i Schematic of the synthesis route of HCNFs.  j Electrochemical performances of CNPs and HCNFs electrodes for SIBs. Reproduced with permission from Ref. [148].  Copyright 2019, Royal Society of Chemistry

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SIBs [143, 144, 188–190]. For example, Dong et al. used the polymethyl methacrylate (PMMA) spheres templates to synthesize S/N-co-doped hollow carbon spheres (SN-HCSs), which showed excellent rate capability (110 mAh g⁻¹ at 10 A g⁻¹) and cycling performance (2000 cycles) [145].

N-containing hollow carbon microspheres (N-HCSs), made by using modified SiO₂ as the template and RF the carbon precursor, displayed a reversible capacity of 114 mAh g⁻¹ at a high current density of 10 A g⁻¹, and long-term cycle stability (> 1200 cycles) [146].

Hollow carbon nanowires and nanofibers have also been used as electrode materials for SIBs [191–194]. For example, Cao and co-workers fabricated hollow carbon nanowires (HCNWs) via pyrolyzation of the hollow polyaniline nanowire precursors [147]. The HCNWs showed a tube-like structure with an outer diameter of ~150 nm and an inner diameter of 20–40 nm (Fig. 9g, h). They exhibited a high reversible specific capacity of 251 mAh g⁻¹, when used as electrodes in SIBs. Besides, hollow carbon nanofibers (HCNFs) have been prepared by a sacrifice template (PMMA), followed by pyrolyzation of the polyaniline hollow nanofiber precursors (Fig. 9i) [148], showing a superior electrochemical performance, when used as anode materials in SIBs (Fig. 9j), e.g., a high reversible capacity of 326 mAh g⁻¹ and good capacity retention of 70% after 5000 cycles. Liang and Yang et al. synthesized N/P co-doped hollow carbon nanofibers and N/S dual-doped hollow carbon fibers, which were employed as the anodes in SIBs [149, 150]. Some resin and biomass-derived hollow carbon materials have been reported for SIBs. For instance, Shen and co-workers synthesized the polyhedral-shaped hollow porous carbon through Ni-ion exchanged resin, together with the carbonization and activation processes [151]. Li et al. used the rape pollen grains as the carbon precursors to acquire 3D hollow reticulate hard carbon through the hydrothermal and high-temperature pretreatment [152]. When employed as the anode in SIBs, this biomass-derived hollow carbon realized an outstanding capacity retention of 90% after 1000 cycles.

3.3 Potassium-Ion Batteries

Recently, potassium-ion batteries (PIBs) have attracted attention as promising alternatives to LIBs and SIBs. In particular, PIBs are expected to offer a higher operation potential in wider voltage range, compared to SIBs. Al-K intermetallic compounds would not be formed during charge–discharge processes, and thus, the low-cost Al foil can be used as the current collector for both cathode and anode electrodes in PIBs. Up to now, there have been reports on hollow carbon materials that are used as active materials for PIBs. For instance, Mitlin and co-workers proposed the sulfur-grafted hollow carbon spheres (SHCS) as anode materials for PIBs [156]. These SHCS were synthesized via a sulfuration strategy, with RF resin as the carbon source, sulfur powder as the sulfur source, and silica sphere as the hard template (Fig. 10a). They showed a monodispersed hollow sphere nanostructure, with a rather uniform diameter (~400 nm) and thickness (~40 nm) (Fig. 10b, c). There is an amorphous structure observed, and the C, O, S elements were seen to evenly distribute in the carbon skeleton (Fig. 10d, e). Benefiting from a high amount of sulfur-grafted (38 wt%) and hollow structure, the SHCS electrode displayed an impressive electrochemical performance for PIBs (Fig. 10f). They can deliver an ultrahigh reversible capacity of 581 mAh g⁻¹ and an excellent capacity retention of 93% after 1000 cycles. Activated hollow carbon nanospheres (AHCSs) have been synthesized and used as anode materials for PIBs, with RF as the carbon source and SiO₂ as the template [157]. Recently, Chen et al. utilized PDA as both the carbon and N-doping sources and silica spheres as the template in preparing N-doped hollow carbon nanospheres (N-NHCMs), which gave a high reversible capacity of 154 mAh g⁻¹ (1.0 A g⁻¹ current density) over 2500 cycles, when employed as the anode electrode in PIBs [158].

Taking the integrity and effectiveness of structures into consideration, the cross-linked hollow structure can not only improve the structural stability, but also increase the electron and ion transfer rate of materials. In view of this, Wan and co-workers have proposed a structural engineering strategy to design carbon materials such that they display a hollow interconnected neuron-like carbon architecture (HINCA) [159]. Such a structure was prepared by high-temperature carbonization of a commercial RF resin foam. There was structural transformation, as shown in Fig. 10g–i, where the SEM images of the HINCA-type products showed a morphological change at different treatment temperatures of 365, 400, and 450 °C. The inner cavity increased, and the wall thickness shrunk with the increase in temperatures. The effect of heating rate (Fig. 10j–l) did not appear to affect the interconnected architecture, as shown for those at different heating rates...
50 µm

10 nm

5 µm

100 nm

5 µm

C

strategy [160]. The as-fabricated CHMBs electrodes

low multihole carbon bowls (CHMBs) by hydrothermal
lar structural design, Qin and co-workers obtained hol-

tained 72.1% of capacity after 500 cycles. With a simi-
la reversible capacity of 340 mAh g−1 at 0.1 C and main-
electrode for PIBs (Fig. 10m). In particular, it delivered
compared with the solid carbon foam and power carbon
temperature was 1300 °C, the as-fabricated HINCA-type

k

0.5,

10,

and
temperature rates of

15 °C min−1.

400,

and

VCH. SEM images of morphological change with temperatures of

h

365,

i

450 °C. SEM images of the carbon products with heating

carbonization

defined by hydrothermal carbonization coupled with a soft template (emulsion)
strategy [160]. The as-fabricated CHMBs electrodes
showed a high specific capacity of 304 mAh g−1 at 0.1 A
g−1 and ultra-long cycling stability (1000 cycles). More
recently, Mai et al. synthesized polycrystalline soft carbon
semi-hollow microrods, which gave an impressive reversible capacity of 314 mAh g−1, when used as an anode for
PIBs [161].

3.4 Lithium–Sulfur Batteries

Lithium–sulfur batteries (LSBs) are among the most prom-
ising next-generation batteries systems, owing to their high
theoretical specific capacity (1675 mAh g−1), where the
sulfur cathode also offers other advantages, including an
abundant source, low cost, and environmental friendliness.
However, LSBs face challenges in practical sense, such as
a low electronic conductivity and large volume expansion
of the sulfur cathode, the dissolution and shuttle effect of

Fig. 10  a Illustration of the synthesis route of SHCS. b, c TEM images, d HRTEM image, and e HAADF image and elements mapping of
SHCS. f Electrochemical performance of SHCS electrodes for PIBs. Reproduced with permission from Ref. [156]. Copyright 2019, Wiley–
VCH. SEM images of morphological change with temperatures of g 365, h 400, and i 450 °C. SEM images of the carbon products with heating
temperature rates of j 0.5, k 10, and l 15 °C min−1. m Electrochemical performance of the HINCA-type, solid carbon foam, and carbon powder electrodes for PIBs. Reproduced with permission from Ref. [159]. Copyright 2018, American Chemical Society

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polysulfide, leading to a rapid capacity fading and poor cycle stability, together with low Coulombic efficiency. To solve some of these problems, NHCMs have been employed as host materials for sulfur cathode, owing to their good electronic conductivity and tailored shell structures. Indeed, several NHCMs have been reported as host materials for application in LSBs, including those hollow carbon nanospheres, hollow carbon nanotubes/nanofibers, hollow carbon nanobowls, hollow carbon foams, and hollow carbon polyhedrons [6, 10, 11].

Among them, hollow carbon nanospheres are the most commonly employed host materials for LSBs, owing to the large cavity that can effectively accommodate the large volume expansion and shuttle effect of polysulfides during the charge–discharge processes [195–205]. For instance, Wang et al. synthesized the hollow nitrogen-doped carbon (HNPC) by anion exchange and subsequent pyrolysis, using rhombic dodecahedral ZIF-8 as the core and imidazolium-based ionic polymers as the shell layer (Fig. 11a) [165]. The HNPC-900 (carbonization at 900 °C) thus made showed a 3D hollow nanosphere network (Fig. 11b–d), which was a desirable structure for sulfur loading. The HNPC-900 electrode delivered a superior electrochemical performance compared with HNPC-800 and HNPC-1000 in LSBs (Fig. 11e), including an excellent reversible capacity of 562 mAh g−1 at 2 C and prolonged cycle stability of 800 cycles. Recently, Shao et al. presented a dual template-assisted strategy to prepare hollow carbon nanospheres (HCS) with diameters of ~ 300 nm [166], which was then employed as sulfur host materials for LSBs. It exhibited a high reversible capacity of 585 mAh g−1 at 2 C and long cycle stability of 600 cycles. Notably, the hollow carbon nanospheres were also reported to decorate separators in LSBs. For example, Zhang and co-workers designed the separator coated with the N-doped porous hollow carbon nanosphere (NHC) to improve the utilization of sulfur cathode and suppress the shuttle effect of polysulfides [167]. They found that the NHC decorated separator could achieve superior electrochemical performance, including a high reversible capacity of 720 mAh g−1 at 5 C and an outstanding cycle lifespan of 500 cycles.

In addition to hollow carbon nanospheres, hollow carbon nanotubes/nanofibers have also been reported as favorable host materials for LSBs [169–172]. For example, Yu and co-workers employed an electrospinning strategy to fabricate hollow carbon nanobubbles on porous carbon nanofibers (CHNBs@PCNFs) [206], which are shown in Fig. 11f–i. In the electrospun PVA-LiN3 nanofibers, the porous hollow carbon nanobubbles were well attached to the surface of hollow carbon nanofibers. Han et al. developed hollow N-doped carbon polyhedrons (HNC) as the host of the sulfur cathode, which was fabricated via chemical etching and carbonization process (Fig. 11j) [168]. Such electrode realized a high sulfur loading of ~72 wt% and an impressive reversible capacity of 501.3 mAh g−1 at 1 C, together with a long cycle life (500 cycles). The HNC also showed a strong chemical interaction with polysulfides by the visualized measurement of S@HNC and S-NC electrodes during the discharge process (Fig. 11k). Other hollow carbon nanostructures, such as hollow carbon nanorods [173], hollow carbon nanobowls [174], hollow carbon foams [175], and hollow carbon nanoparticles [176], have been also employed as host materials for the sulfur cathode.

4 Conclusion and Outlook

In summary, we have reviewed the ongoing progresses of exploring nanohollow carbon materials (NHCMs), including their synthesis strategies, different types of morphologies, and performance in several types of rechargeable batteries. For each of the morphologies of hollow nanospheres, nanopolyhedrons, and nanofibers, a proper tuning in the key structural features by processing controls, NHCMs show great potential as the electrode materials in rechargeable batteries, including LIBs, SIBs, PIBs, and LSBs. In addition to being electrodes by themselves, NHCMs also act as an efficient supporting substrate for other active materials, improving the loading, overall electronic conductivity, and mechanical stability, leading to faster reaction kinetics, better performance, and long cycle ability [207]. Although considerable progress has been made so far, in almost all aspects, attempted by various strategies as described in this overview, there are several unsolved issues and challenges, which should be addressed further, especially for developing large-scale production at low cost, and application in energy storage.

For NHCMs fabrication, various synthesis strategies (hard templating, soft templating, template-free, MOF-derived, and electrospinning) have been developed. In particular, the hard template methods are currently the most widely used, giving rise to various desired key structure features. However, the synthesis processes of hard templates are
multi-steps and time-consuming, owing to the pre-making and removal of templates, together with the use of high-cost carbon precursors. The rather tedious, high-cost, and low-yield multi-steps are the apparent disadvantages. On the other hand, the various soft template methods are relatively simple and can be applied on a large scale by eliminating the template etching process. However, the morphologies and key features of the as-fabricated NHCMs are usually difficult to control. The newly emerged template-free approaches give opportunities to synthesize NHCMs, by the combination of facile processing, low cost, and generally high uniformity. For example, aerosol spraying is a typical template-free approach, in which the high production yield, cost-effectiveness, and continuous process enable a better control in the desired morphologies and compositions. Nevertheless, most of the template-free methods are relatively immature up to now. Therefore, further development of the existing template-free methods and devising new ones shall be
pursued for NHCMs, especially those leading to the desired hollow structures. In this connection, metal–organic frameworks derived nanohollow carbon polyhedrons and electrospun nanohollow carbon nanofibers are among the exciting ongoing research and development. There is no doubt that more effective strategies will appear in the coming years, and they will be explored for applications in energy storage and other related devices.

For NHCMs applications, the first key issue is the relatively low volume energy density that can be derived, because of their low tap density. Therefore, new hollow nanostructures shall be designed such that the cavities in NHCMs will be used as much as possible. For example, the development of multi-shelled and yolk–shell structures can be a suitable approach to improve the volumetric energy density, with other advantages. Secondly, the storage mechanisms of NHCMs when employed as the electrode materials for rechargeable batteries need to be understood thoroughly. In addition, the key structural features such as the inter-layer spacing of NHCMs shall be different for the respective Li-ion, Na-ion, and K-ion batteries, owing to their different ionic radii and diffusion rates. Also, the specific energy storage (Li⁺, Na⁺, K⁺) mechanisms would be different among them. For example, for rechargeable LSBs, the HNCS can be used as a host material to effectively fill the sulfur cathode and suppress the shuttle effect of polysulfides. Therefore, the corresponding energy storage mechanisms need to be properly investigated and understood with the help of some advanced in situ characterizations, such as in situ XRD, SEM, TEM, AFM, together with some theoretical calculations, including the density functional theory (DFT), and molecular dynamics (MD). Thirdly, heteroatom doping (N, O, B, S, P, etc.) has been widely applied in NHCMs to improve their electrochemical performance and reaction kinetics. The heteroatom types, corresponding doping levels, and their impact on the structures and properties of NHCMs need to be further explored. Fourthly, the NHCMs electrodes often exhibit certain initial irreversibility, which would severely consume ions from the electrolyte and cathodes, leading to low Coulombic efficiency and poor cycle lifespan. Thus, it would be of value to develop an appropriate ion pre-embedding technique for the full-battery systems. We hope that this review can provide an avenue for better understanding of the design and synthesis of nanohollow carbon materials and stimulate greater interests and efforts toward their functionalization and applications.

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References

1. B. Hu, K. Wang, L.H. Wu, S.H. Yu, M. Antonietti et al., Engineering carbon materials from the hydrothermal carbonization process of biomass. Adv. Mater. 22(7), 813–828 (2010). https://doi.org/10.1002/adma.200902812
2. Y. Liu, J. Goebl, Y. Yin, Templated synthesis of nanostructured materials. Chem. Soc. Rev. 42(7), 2610–2653 (2013). https://doi.org/10.1039/C2CS35369E
3. C. Wang, Y.V. Kaneti, Y. Bando, J. Lin, C. Liu et al., Metal-organic framework-derived one-dimensional porous or hollow carbon-based nanofibers for energy storage and conversion. Mater. Horiz. 5(3), 394–407 (2018). https://doi.org/10.1039/C8MH00133B
4. J. Jiang, Y. Zhang, P. Nie, G. Xu, M. Shi et al., Progress of nanostructured electrode materials for supercapacitors. Adv. Sustain. Syst. 2(1), 1700110 (2018). https://doi.org/10.1002/adsu.201700110
5. S. Li, A. Pasc, V. Fierro, A. Celzard, Hollow carbon spheres, synthesis and applications-a review. J. Mater. Chem. A 4(33), 12686–12713 (2016). https://doi.org/10.1039/C6TA03802F
6. Z. Li, H.B. Wu, X.W.D. Lou, Rational designs and engineering of hollow micro-/nanostructures as sulfur hosts for advanced lithium-sulfur batteries. Energy Environ. Sci. 9(10), 3061–3070 (2016). https://doi.org/10.1039/C6EE02364A
7. X. Liu, W.H. Lai, S. Chou, The application of hollow micro-/nanostructured cathodes for sodium-ion batteries.
11. A. Fu, C. Wang, F. Pei, J. Cui, X. Fang et al., Recent advances in hollow porous carbon materials for lithium-sulfur batteries. Adv. Energy Mater. 9(17), 1803900 (2019). https://doi.org/10.1002/aenm.201803900

12. H. Fan, F. Ran, X. Zhang, H. Song, X. Niu et al., Hollow carbon microspheres/MnO2 nanosheets composites: hydrothermal synthesis and electrochemical behaviors. Nano-Micro Lett. 7(1), 59–67 (2015). https://doi.org/10.1007/s40820-014-0019-z

13. X.L. Ji, A paradigm of storage batteries. Energy Environ. Sci. 12(11), 3203–3224 (2019). https://doi.org/10.1039/c9ee02356a

14. J. Jiang, Z. Pan, Z. Kou, P. Nie, C. Chen et al., Lithiophilic polymer interphase anchored on laser-punched 3D holey Cu matrix enables uniform lithium nucleation leading to superstable lithium metal anodes. Energy Storage Mater. 29, 84–91 (2020). https://doi.org/10.1016/j.ensm.2020.04.006

15. J. Jiang, P. Nie, B. Ding, W. Wu, Z. Chang et al., Effect of graphene modified Cu current collector on the performance of Li2Ti3O7 anode for lithium-ion batteries. ACS Appl. Mater. Interfaces 8(45), 30926–30932 (2016). https://doi.org/10.1021/acsami.6b03038

16. W. Chen, M. Wan, Q. Liu, X. Xiong, F. Yu et al., Heteroatom-doped carbon materials: synthesis, mechanism, and application for sodium-ion batteries. Small Methods 3(4), 1800323 (2019). https://doi.org/10.1002/smtd.201900323

17. H. Geng, Y. Peng, L. Qu, H. Zhang, M. Wu, Structure design and composition engineering of carbon-based nanomaterials for lithium energy storage. Adv. Energy Mater. 10(10), 1903030 (2020). https://doi.org/10.1002/aenm.201903030

18. L. Wang, J. Han, D. Kong, Y. Tao, Q. Yang, Enhanced roles of carbon architectures in high-performance lithium-ion batteries. Nano-Micro Lett. 11(1), 5 (2019). https://doi.org/10.1007/s40820-018-0233-1

19. J. Jiang, P. Nie, B. Ding, Y. Zhang, G. Xu et al., Highly stable lithium ion capacitor enabled by hierarchical polyimide derived carbon microspheres combined with 3D current collectors. J. Mater. Chem. A 5(44), 23283–23291 (2017). https://doi.org/10.1039/C7TA05972H

20. C. Wang, J. Kim, J. Tang, M. Kim, H. Lim et al., New strategies for novel MOF-derived carbon materials based on nanoarchitectures. Chem 6(1), 19–40 (2020). https://doi.org/10.1016/j.chempr.2019.09.005

21. F. Marpaung, M. Kim, J.H. Khan, K. Konstantinov, Y. Yamauchi et al., Metal-organic framework (MOF)-derived nanoporous carbon materials. Chem. Asian J. 14(9), 1331–1343 (2019). https://doi.org/10.1002/asia.201900026

22. J. Yin, W. Zhang, N.A. Alhebshi, N. Salah, H.N. Alshareef, Synthesis strategies of porous carbon for supercapacitor applications. Small Methods 4(3), 1900853 (2020). https://doi.org/10.1002/smtd.201900853

23. F. Caruso, R.A. Caruso, H. Möhwald, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating. Science 282(5391), 1111–1114 (1998). https://doi.org/10.1126/science.282.5391.1111

24. J. Jiang, Y. Zhang, Y. An, L. Wu, Q. Zhu et al., Engineering ultrathin MoS2 nanosheets anchored on N-doped carbon microspheres with pseudocapacitive properties for high-performance lithium-ion capacitors. Small Methods 3(7), 1900081 (2019). https://doi.org/10.1002/smtd.201900081

25. W.J. Lee, J. Lim, S.O. Kim, Nitrogen dopants in carbon nanomaterials: defects or a new opportunity? Small Methods 1(1–2), 1600014 (2017). https://doi.org/10.1002/smtd.201600014

26. K.L. Zhang, X.H. Xia, S.J. Deng, Y. Zhong, D. Xie et al., Nitrogen-doped sponge Ni fibers as highly efficient electrocatalysts for oxygen evolution reaction. Nano-Micro Lett. 11(1), 21 (2019). https://doi.org/10.1002/smtd.2018019-0253-5

27. Z. Wang, H. Gao, Q. Zhang, Y. Liu, J. Chen et al., Recent advances in 3D graphene architectures and their composites for energy storage applications. Small 15(3), 1803858 (2019). https://doi.org/10.1002/smtd.201803858

28. K. Chen, L. Shi, Y. Zhang, Z. Liu, Scalable chemical-vapour-deposition growth of three-dimensional graphene materials towards energy-related applications. Chem. Soc. Rev. 47(9), 3018–3036 (2018). https://doi.org/10.1039/C7CS00852J

29. J. Mao, J. Iocozzia, J. Huang, K. Meng, Y. Lai et al., Graphene aerogels for efficient energy storage and conversion. Energy Environ. Sci. 11(4), 772–799 (2018). https://doi.org/10.1039/C7EE03031B

30. Y. Zhang, J. Jiang, Y. An, L. Wu, H. Dou et al., Sodium ion capacitors: materials, mechanism and challenges. ChemSusChem 13(10), 2522–2539 (2020). https://doi.org/10.1002/cssc.201903440

31. K. Li, J. Zhang, Recent advances in flexible supercapacitors based on carbon nanotubes and graphene. Sci. China Mater. 61(2), 210–232 (2018). https://doi.org/10.1007/s40843-017-9154-2

32. X. Li, Y. Chen, H. Huang, Y. Mai, L. Zhou, Electrospun carbon-based nanostructured electrodes for advanced energy storage-a review. Energy Storage Mater. 5, 58–92 (2016). https://doi.org/10.1016/j.ensm.2016.06.002

33. H. Feng, L. Tang, G. Zeng, J. Tang, Y. Deng et al., Carbon-based core-shell nanostructured materials for electrochemical energy storage. J. Mater. Chem. A 6(17), 7310–7337 (2018). https://doi.org/10.1039/C8TA01257A
34. L. Jiang, X. Yuan, J. Liang, J. Zhang, H. Wang et al., Nanostructured core-shell electrode materials for electrochemical capacitors. J. Power Sources 331, 408–425 (2016). https://doi.org/10.1016/j.jpowsour.2016.09.054

35. P. Russo, A. Hu, G. Compagnini, Synthesis, properties and potential applications of porous graphene: a review. Nano-Micro Lett. 5(4), 260–273 (2013). https://doi.org/10.1007/BF03353757

36. O. Noonan, H. Zhang, H. Song, C. Xu, X. Huang et al., In situ Stöber templating: facile synthesis of hollow mesoporous carbon spheres from silica-polymer composites for ultra-high level in-cavity adsorption. J. Mater. Chem. A 4(23), 9063–9071 (2016). https://doi.org/10.1039/C6TA02265K

37. Y. Han, X. Dong, C. Zhang, S. Liu, Hierarchical porous carbon hollow-spheres as a high performance electrical double-layer capacitor material. J. Power Sources 211, 92–96 (2012). https://doi.org/10.1016/j.jpowsour.2012.03.053

38. G. Ferrero, A. Fuertes, M. Sevilla, N-doped porous carbon capsules with tunable porosity for high-performance supercapacitors. J. Mater. Chem. A 3(6), 2914–2923 (2015). https://doi.org/10.1039/C4TA06022A

39. A. Chen, Y. Yu, H. Lv, Y. Wang, S. Shen et al., Thin-walled, mesoporous and nitrogen-doped hollow carbon spheres using ionic liquids as precursors. J. Mater. Chem. A 1(4), 1045–1047 (2013). https://doi.org/10.1039/C2TA01013E

40. C. Wang, F. Wang, Z. Liu, Y. Zhao, Y. Liu et al., N-doped carbon hollow microspheres for metal-free quasi-solid-state full sodium-ion capacitors. Nano Energy 41, 674–680 (2017). https://doi.org/10.1016/j.nanoen.2017.10.025

41. B.Y. Guan, L. Yu, X.W. Lou, Chemically assisted formation of monolayer colloidosomes on functional particles. Adv. Mater. 28(43), 9596–9601 (2016). https://doi.org/10.1002/adma.201603622

42. M. Kim, S.B. Yoon, K. Sohn, J.Y. Kim, C.H. Shin et al., Synthesis and characterization of spherical carbon and polymer capsules with hollow macroporous core and mesoporous shell structures. Microporous Mesoporous Mater. 63(1–3), 1–9 (2003). https://doi.org/10.1016/S1387-1811(03)00410-4

43. A.B. Fuertes, P. Valle-Vigón, M. Sevilla, One-step synthesis of silica@resorcinol–formaldehyde spheres and their application for the fabrication of polymer and carbon capsules. Chem. Commun. 48(49), 6124–6126 (2012). https://doi.org/10.1039/C2CC32552G

44. X. Fang, J. Zang, X. Wang, M.S. Zheng, N. Zheng, A multiple coating route to hollow carbon spheres with foam-like shells and their applications in supercapacitor and confined catalysis. J. Mater. Chem. A 2(17), 6191–6197 (2014). https://doi.org/10.1039/C3TA14881E

45. H. Zhang, M. Yu, H. Song, O. Noonan, J. Zhang et al., Self-organized mesostructured hollow carbon nanoparticles via a surfactant-free sequential heterogeneous nucleation pathway. Chem. Mater. 27(18), 6297–6304 (2015). https://doi.org/10.1021/acs.chemmater.5b01993

46. F. Su, X. Zhao, Y. Wang, L. Wang, J.Y. Lee, Hollow carbon spheres with a controllable shell structure. J. Mater. Chem. 16(45), 4413–4419 (2006). https://doi.org/10.1039/C5BM01993

47. X. Chen, K. Kierzek, K. Cendrowski, I. Pelech, X. Zhao et al., CVD generated mesoporous hollow carbon spheres as supercapacitors. Colloids Surf. A 396, 246–250 (2012). https://doi.org/10.1016/j.colsurfa.2012.01.002

48. X. Chen, K. Kierzek, Z. Jiang, H. Chen, T. Tang et al., Synthesis, growth mechanism, and electrochemical properties of hollow mesoporous carbon spheres with controlled diameter. J. Phys. Chem. C 115(36), 17717–17724 (2011). https://doi.org/10.1021/jp205257u

49. M.M. Titirici, A. Thomas, M. Antonietti, Replication and coating of silica templates by hydrothermal carbonization. Adv. Funct. Mater. 17(6), 1010–1018 (2007). https://doi.org/10.1002/adfm.200600501

50. J. Fu, Q. Xu, J. Chen, Z. Chen, X. Huang et al., Controlled fabrication of uniform hollow core porous shell carbon spheres by the pyrolysis of core/shell polystyrene/cross-linked polyphosphazene composites. Chem. Commun. 46(35), 6563–6565 (2010). https://doi.org/10.1039/C0CC1185A

51. A. Chen, Y. Li, Y. Yu, Y. Li, K. Xia et al., Synthesis of hollow mesoporous carbon spheres via “dissolution-capture” method for effective phenol adsorption. Carbon 103, 157–162 (2016). https://doi.org/10.1016/j.carbon.2016.02.091

52. L.K. Gil-Herrera, Á. Blanco, B.H. Juárez, C. López, Seeded synthesis of monodisperse core-shell and hollow carbon spheres. Small 12(32), 4357–4362 (2016). https://doi.org/10.1002/smll.201600902

53. A.H. Lu, T. Sun, W.C. Li, Q. Sun, F. Han et al., Synthesis of discrete and dispersible hollow carbon nanospheres with high uniformity by using confined nanospace pyrolysis. Angew. Chem. Int. Ed. 50(49), 11765–11768 (2011). https://doi.org/10.1002/anie.201105486

54. J. Han, G. Xu, B. Ding, J. Pan, H. Dou et al., Porous nitrogen-doped hollow carbon spheres derived from polyaniline for high performance supercapacitors. J. Mater. Chem. A 2(15), 5352–5357 (2014). https://doi.org/10.1039/C3TA15271E

55. L. Xin, R. Chen, Q. Liu, J. Liu, Z. Li et al., Composites of hierarchical metal-organic framework derived nitrogen-doped porous carbon and interpenetrating 3D hollow carbon spheres from lotus pollen for high-performance supercapacitors. New J. Chem. 41(21), 12835–12842 (2017). https://doi.org/10.1039/C7NJ02427D

56. X. He, H. Sun, M. Zhu, M. Yaseen, D. Liao et al., N-doped porous graphitic carbon with multi-flaky shell hollow structure prepared using a green and ‘useful’ template of CaCO3 for VOC fast adsorption and small peptide enrichment. Chem. Commun. 53(24), 3442–3445 (2017). https://doi.org/10.1039/C7CC00242D

57. W. Liu, X. Huang, H. Wei, K. Chen, J. Gao et al., Facile preparation of hollow crosslinked polyphosphazene submicrospheres with mesoporous shells. J. Mater. Chem. 21(34), 12964–12968 (2011). https://doi.org/10.1039/C1JM11802A

58. H. Guo, B. Ding, J. Wang, Y. Zhang, X. Hao et al., Template-induced self-activation route for nitrogen-doped...
hierarchically porous carbon spheres for electric double layer capacitors. Carbon 136, 204–210 (2018). https://doi.org/10.1016/j.carbon.2018.04.079
59. J. Liu, M. Shao, Q. Tang, X. Chen, Z. Liu, A medial-reduction route to hollow carbon spheres. Carbon 41(8), 1682–1685 (2003). https://doi.org/10.1016/S0008-6223(03)00143-X
60. L. Shi, H. Lin, K. Bao, J. Cao, Y. Qian, Controlled growth of carbon spheres through the Mg-reduction route. Nanoscale Res. Lett. 5(1), 20 (2010). https://doi.org/10.1007/s11671-009-9436-1
61. G. Hu, D. Ma, M. Cheng, L. Liu, X. Bao, Direct synthesis of uniform hollow carbon spheres by a self-assembly template approach. Chem. Commun. 17, 1948–1949 (2002). https://doi.org/10.1039/B205723A
62. Z. Bai, Y. Zhang, N. Fan, C. Guo, B. Tang, One-step synthesis of ZnO@C nanospheres and their enhanced performance for lithium-ion batteries. Mater. Lett. 119, 16–19 (2014). https://doi.org/10.1016/j.matlet.2013.12.060
63. R. Liu, N. Lun, Y. Qi, H. Zhu, Y. Bai et al., Synthesis of hollow carbon sphere/ZnO@C composite as a light-weight microwave absorber. J. Phys-D Appl. Phys. 44(26), 265502 (2011). https://doi.org/10.1088/0022-3727/44/26/265502
64. F. Wang, L. Pang, Y. Jiang, B. Chen, D. Lin et al., Simple synthesis of hollow carbon spheres from glucose. Mater. Lett. 63(29), 2564–2566 (2009). https://doi.org/10.1016/j.matlet.2009.09.008
65. J. Liu, T. Yang, D. Wang, G.Q.M. Lu, D. Zhao et al., A facile soft-template synthesis of mesoporous polymeric and carbonaceous nanospheres. Nat. Commun. 4(1), 1–7 (2013). https://doi.org/10.1038/ncomms3798
66. B.Y. Guan, L. Yu, X.W. Lou, Formation of asymmetric bowl-like mesoporous particles via emulsion-induced interface anisotropic assembly. J. Am. Chem. Soc. 138(35), 11306–11311 (2016). https://doi.org/10.1021/jacs.6b06558
67. D. Liu, N. Xue, L. Wei, Y. Zhang, Z. Qin et al., Surfactant assembly within picking emulsion droplets for fabrication of interior-structured mesoporous carbon microspheres. Angew. Chem. Int. Ed. 130(34), 11065–11070 (2018). https://doi.org/10.1002/ange.201805022
68. B.Y. Guan, S.L. Zhang, X.W. Lou, Realization of walnut-shaped particles with macro-/mesoporous open channels through pore architecture manipulation and their use in electrocatalytic oxygen reduction. Angew. Chem. Int. Ed. 57(21), 6176–6180 (2018). https://doi.org/10.1002/anie.201801876
69. Y. Yang, S. Jin, Z. Zhang, Z. Du, H. Liu et al., Nitrogen-doped hollow carbon nanospheres for high-performance Li-ion batteries. ACS Appl. Mater. Interfaces. 9(16), 14180–14186 (2017). https://doi.org/10.1021/acsami.6b14840
70. C. Yuan, X. Liu, M. Jia, Z. Luo, J. Yao, Facile preparation of N- and O-doped hollow carbon spheres derived from poly (o-phenylenediamine) for supercapacitors. J. Mater. Chem. A 3(7), 3409–3415 (2015). https://doi.org/10.1039/C4TA06411A
71. H. Zhang, F. Ye, H. Xu, L. Liu, H. Guo, Synthesis of carbon hollow particles by a simple inverse-emulsion method. Mater. Lett. 64(13), 1473–1475 (2010). https://doi.org/10.1016/j.matlet.2010.03.065
72. Z. Wen, Q. Wang, Q. Zhang, J. Li, Hollow carbon spheres with wide size distribution as anode catalyst support for direct methanol fuel cells. Electrochem. Commun. 9(8), 1867–1872 (2007). https://doi.org/10.1016/j.elecom.2010.03.065
73. X. Sun, Y. Li, Hollow carbonaceous capsules from glucose solution. J. Colloid Interface Sci. 291(1), 7–12 (2005). https://doi.org/10.1016/j.jcis.2005.04.010
74. Y. Qu, Z. Zhang, X. Wang, Y. Lai, Y. Liu et al., A simple SDS-assisted self-assembly method for the synthesis of hollow carbon nanospheres to encapsulate sulfur for advanced lithium-sulfur batteries. J. Mater. Chem. A 4(45), 14306–14310 (2013). https://doi.org/10.1039/C3TA13306K
75. D. Fujikawa, M. Uota, G. Sakai, T. Kijima, Shape-controlled synthesis of nanocarbons from resorcinol-formaldehyde nanopolymers using surfactant-templated vesicular assemblies. Carbon 45(6), 1289–1295 (2007). https://doi.org/10.1016/j.carbon.2007.01.020
76. D. Tashima, E. Yamamoto, N. Kai, D. Fujikawa, G. Sakai et al., Double layer capacitance of high surface area carbon nanospheres derived from resorcinol-formaldehyde polymers. Carbon 49(14), 4848–4857 (2011). https://doi.org/10.1016/j.carbon.2011.07.005
77. H. Sun, Y. Zhu, S. Yang, Y. Wang, Y. Wu et al., Template-free fabrication of nitrogen-doped hollow carbon spheres for high-performance supercapacitors based on a scalable homopolymer vesicle. J. Mater. Chem. A 4(31), 12088–12097 (2016). https://doi.org/10.1039/C6TA04330E
78. J. Jiang, J. Yuan, P. Nie, Q. Zhu, C. Chen et al., Hierarchical N-doped hollow carbon microspheres as advanced materials for high-performance lithium-ion capacitors. J. Mater. Chem. A 7(8), 3956–3966 (2020). https://doi.org/10.1039/C9TA08676E
79. W. Sun, M. Chen, S. Zhou, L. Wu, Facile fabrication of carbon spheres with tunable morphologies from novel polymeric carbon precursors. Langmuir 30(40), 12011–12017 (2014). https://doi.org/10.1021/la5026476
80. K. Niwase, T. Homae, K. Nakamura, K. Kondo, Generation of giant carbon hollow spheres from C60 fullerene by shock-compression. Chem. Phys. Lett. 362(1–2), 47–50 (2002). https://doi.org/10.1016/S0009-2614(02)00997-1
81. F. Ma, L. Sun, H. Zhao, Q. Li, L. Huo et al., Supercapacitor performance of hollow carbon spheres by direct pyrolysis of melamine-formaldehyde resin spheres. Chem. Res. Chin. Univ. 29(4), 735–742 (2013). https://doi.org/10.1007/s40099-2014-03181-9
82. J. Zhou, Z. Sun, M. Chen, J. Wang, W. Qiao et al., Macroporous and mechanically robust hollow carbon spheres with superior oil adsorption and light-to-heat evaporation properties. Adv. Funct. Mater. 26(29), 5368–5375 (2016). https://doi.org/10.1002/adfm.201600564
83. H. Xu, J. Guo, K.S. Suslick, Porous carbon spheres from energetic carbon precursors using ultrasonic spray pyrolysis. Adv. Mater. 24(45), 6028–6033 (2012). https://doi.org/10.1002/adma.201201915
84. P. Nie, G. Xu, J. Jiang, H. Dou, Y. Wu et al., Aerosol-spray pyrolysis toward preparation of nanostructured materials for batteries and supercapacitors. Small Methods 2(2), 1700272 (2018). https://doi.org/10.1002/smtd.201700272

85. J.S. Park, J.K. Kim, J.H. Hong, J.S. Cho, S.K. Park et al., Advances in the synthesis and design of nanostructured materials by aerosol spray processes for efficient energy storage. Nanoscale 11(41), 19012–19057 (2019). https://doi.org/10.1039/C9NR05575D

86. T. Zheng, J. Zhan, J. Pang, G.S. Tan, J. He et al., Mesoporous carbon nanocapsules from enzymatically polymerized poly(4-ethylphenol) confined in silica aerosol particles. Adv. Mater. 18(20), 2735–2738 (2006). https://doi.org/10.1002/adma.200600808

87. S. Kim, E. Shibata, R. Sergiienko, T. Nakamura, Purification and separation of carbon nanocapsules as a magnetic carrier for drug delivery systems. Carbon 46(12), 1523–1529 (2008). https://doi.org/10.1016/j.carbon.2008.05.027

88. H. Okuno, E. Grivei, F. Fabry, T.M. Gruenberger, J. Gonzalez-Aguilar et al., Synthesis of carbon nanotubes and nano-necklaces by thermal plasma process. Carbon 42(12–13), 2543–2549 (2004). https://doi.org/10.1016/j.carbon.2003.05.037

89. P. González-García, E. Urones-Garrote, D. Ávila-Brande, L. Otero-Díaz, Carbon particles of variable shape produced by the chlorination of bis(benzene) chromium. J. Organomet. Chem. 740, 141–147 (2013). https://doi.org/10.1016/j.jorganchem.2013.05.011

90. H.-F. Wang, L. Chen, H. Pang, S. Kaska, Q. Xu, MOF-derived electrocatalysts for oxygen reduction, oxygen evolution and hydrogen evolution reactions. Chem. Soc. Rev. 49(5), 1414–1448 (2020). https://doi.org/10.1039/C9CS00960j

91. R.R. Salunkhe, Y.V. Kaneti, J. Kim, J.H. Kim, Y. Yamauchi, Nanoarchitectures for metal-organic framework-derived nanoporous carbons toward supercapacitor applications. Acc. Chem. Res. 49(12), 2796–2806 (2016). https://doi.org/10.1021/acs.accounts.6b00460

92. B. Liu, H. Shioyama, T. Akita, Q. Xu, Metal-organic framework as a template for porous carbon synthesis. J. Am. Chem. Soc. 130(16), 5390–5391 (2008). https://doi.org/10.1021/ja7106146

93. M. Hu, J. Reboul, S. Furukawa, N.L. Torad, Q. Ji et al., Direct carbonization of al-based porous polymer coordination for synthesis of nanoporous carbon. J. Am. Chem. Soc. 134(6), 2864–2867 (2012). https://doi.org/10.1021/ja208940u

94. X. Li, S. Zheng, L. Jin, Y. Li, P. Geng et al., Metal-organic framework-derived carbons for battery applications. Adv. Energy Mater. 8(23), 1800716 (2018). https://doi.org/10.1002/aenm.201800716

95. W. Yang, X. Li, Y. Li, R. Zhu, H. Pang, Applications of metal-organic-framework-derived carbon materials. Adv. Mater. 31(6), 1804740 (2019). https://doi.org/10.1002/adma.201804740

96. C. Liu, X. Huang, J. Wang, H. Song, Y. Yang et al., Hollow mesoporous carbon nanocubes: rigid-interface-induced outward contraction of metal-organic frameworks. Adv. Funct. Mater. 28(6), 1705253 (2018). https://doi.org/10.1002/adfm.201705253

97. H. Zhou, D. He, A.I. Saana, J. Yang, Z. Wang et al., Mesoporous-silica induced doped carbon nanotube growth from metal-organic frameworks. Nanoscale 10(13), 6147–6154 (2018). https://doi.org/10.1039/C8NR00137E

98. T. Feng, M. Zhang, A mixed-ion strategy to construct CNT-decorated Co/N-doped hollow carbon for enhanced oxygen reduction. Chem. Commun. 54(82), 11570–11573 (2018). https://doi.org/10.1039/C8CC05959D

99. M.J. Wang, Z.X. Mao, L. Liu, L. Peng, N. Yang et al., Preparation of hollow nitrogen doped carbon via stresses induced orientation contraction. Small 14(52), 1804183 (2018). https://doi.org/10.1002/smll.201804183

100. J. Wang, X. Luo, C. Young, J. Kim, Y.V. Kaneti et al., A glucose-assisted hydrothermal reaction for directly transforming metal-organic frameworks into hollow carbonaceous materials. Chem. Mater. 30(13), 4401–4408 (2018). https://doi.org/10.1021/acs.chemmater.8b01792

101. W. Zhang, X. Jiang, Y. Zhao, A. Carné-Sánchez, V. Málgras et al., Hollow carbon nanobubbles: monocristalline MOF nanobubbles and their pyrolysis. Chem. Sci. 8(5), 3538–3546 (2017). https://doi.org/10.1039/C6SC04903F

102. X. Wang, Z. Na, D. Yin, C. Wang, Y. Wu et al., Phytic acid-assisted formation of hierarchical porous CoP/C nanoboxes for enhanced lithium storage and hydrogen generation. ACS Nano 12(12), 12238–12246 (2018). https://doi.org/10.1021/acsnano.8b06039

103. J. Zhang, J. Fang, J. Han, T. Yan, L. Shi et al., N, P, S co-doped hollow carbon polyhedra derived from MOF-based core-shell nanocomposites for capacitive deionization. J. Mater. Chem. A 6(31), 15245–15252 (2018). https://doi.org/10.1039/C8TA04813D

104. Y. Chen, S. Ji, S. Zhao, W. Chen, J. Dong et al., Enhanced oxygen reduction with single-atomic-site iron catalysts for a zinc-air battery and hydrogen-air fuel cell. Nat. Commun. 9(1), 1–12 (2018). https://doi.org/10.1038/s41467-018-07850-2

105. W. Ma, N. Wang, T. Tong, L. Zhang, K.-Y.A. Lin et al., Nitrogen, phosphorus, and sulfur tri-doped hollow carbon shells derived from ZIF-67@ poly (cyclotriphosphazene-co-4,4′-sulfonyldiphenol) as a robust catalyst of peroxy-monosulfate activation for degradation of bisphenol a. Carbon 13, 291–303 (2018). https://doi.org/10.1016/j.carbon.2018.05.039

106. V.S. Kale, M. Hwang, H. Chang, J. Kang, S.I. Chae et al., Microporosity-controlled synthesis of heteroatom codoped carbon nanocages by wrap-bake-sublimate approach for flexible all-solid-state-supercapacitors. Adv. Funct. Mater. 28(37), 1803786 (2018). https://doi.org/10.1002/adfm.201803786

107. H. Yang, S.J. Bradley, A. Chan, G.I. Waterhouse, T. Nann et al., Catalytically active bimetallic nanoparticles supported on porous carbon capsules derived from metal-organic framework composites. J. Am. Chem. Soc. 138(36), 11872–11881 (2016). https://doi.org/10.1021/jacs.6b06736
108. P. Ramakrishnan, S.G. Park, S. Shannugam, Three-dimen-
sional hierarchical nitrogen-doped arch and hollow nano-
carbons: morphological influences on supercapacitor applica-
tions. J. Mater. Chem. A 3(31), 16242–16250 (2015). https:
/doi.org/10.1039/C5TA03384E

109. Q. Xu, X. Yu, Q. Liang, Y. Bai, Z.H. Huang et al., Nitro-
gened hollow activated carbon nanofibers as high per-
formance supercapacitor electrodes. J. Electroanal. Chem. 739,
84–88 (2015). https://doi.org/10.1016/j.jelec.
hem.2014.12.027

110. C. Zhan, Q. Xu, X. Yu, Q. Liang, Y. Bai et al., Nitrogen-
rich hierarchical porous hollow carbon nanofibers for high-
performance supercapacitor electrodes. RSC Adv. 6(47),
41473–41476 (2016). https://doi.org/10.1039/C6RA07128G

111. J.G. Kim, H.C. Kim, N.D. Kim, M.S. Khil, N-doped hier-
archical porous hollow carbon nanofibers based on PAN/PVP@SAN
structure for high performance supercapacitor. Compos. B 186,
107825 (2020). https://doi.org/10.1016/j.composites.
b.2020.107825

112. T.H. Le, Y. Yang, L. Yu, T. Gao, Z. Huang et al., Polyimide-
based porous hollow carbon nanofibers for supercapacitor electrod.e
J. Appl. Polym. Sci. 133(19), 43397 (2016). https:
/doi.org/10.1002/app.43397

113. Y. Wang, G. Li, J. Jin, S. Yang, Hollow porous carbon
nanofibers as novel support for platinum-based oxygen
reduction reaction electrocatalysts. Int. J. Hydrogen Energy
42(9), 5938–5947 (2017). https://doi.org/10.1016/j.ijhyd.
ene.2017.02.012

114. T. He, Q. Su, Z. Yildiz, K. Cai, Y. Wang, Ultrastable
fibers with hollow-porous multilayered structure for super-
capacitors. Electrochim. Acta 222, 1120–1127 (2016). https:
/doi.org/10.1016/j.electacta.2016.11.083

115. A. Sharma, Free standing hollow carbon fiber mats for
supercapacitor electrodes. RSC Adv. 6(82), 78528–78537
(2016). https://doi.org/10.1039/C6RA07141E

116. X. Li, X. Chen, Y. Zhao, Y. Deng, J. Zhu et al., Flexible all-
solid-state supercapacitors based on an integrated electrode of hollow N-doped carbon nanofibers embedded with gra-
phene nanosheets. Electrochim. Acta 332, 135398 (2020). https:
/doi.org/10.1016/j.electacta.2019.135398

117. L.-F. Chen, Y. Lu, L. Yu, X.W.D. Lou, Designed formation of hollow particle-based nitrogen-doped carbon nanofibers
for high-performance supercapacitors. Energy Environ. Sci.
10(8), 1777–1783 (2017). https://doi.org/10.1039/C7EE0
0488E

118. C. Wang, C. Liu, J. Li, X. Sun, J. Shen et al., Electrospun
metal-organic framework derived hierarchical carbon
nanofibers with high performance for supercapacitors. Chem.
Commun. 53(10), 1751–1754 (2017). https://doi.org/10.1039/C6CC09832K

119. Y. Sun, R.B. Sills, X. Hu, Z.W. Seh, X. Xiao et al., A bam-
booo-inspired nanostructure design for flexible, foldable, and
stable energy storage devices. Nano Lett. 15(6), 3899–3906 (2015).
https://doi.org/10.1021/acs.nanolett.5b00738

120. L. Wang, G. Zhang, X. Zhang, H. Shi, W. Zeng et al.,
Porous ultrathin carbon nanobubbles formed carbon
nanofiber webs for high-performance flexible supercapacitors.
J. Mater. Chem. A 5(28), 14801–14810 (2017). https:
/doi.org/10.1039/C7TA03445H

121. W. Xie, X. Jiang, T. Qin, H. Yang, D. Liu et al., Inner porous carbon nanofibers as binder-free electrodes for high-
rate supercapacitors. Electrochim. Acta 258, 1064–1071
(2017). https://doi.org/10.1016/j.electacta.2017.11.159

122. L. Zhang, L. Han, S. Liu, C. Zhang, S. Liu, High-perform-
ance supercapacitors based on electrospun multichannel
carbon nanofibers. RSC Adv. 5(130), 107313–107317
(2015). https://doi.org/10.1039/C5RA23338K

123. P. Ramakrishnan, S. Shannugam, Nitrogen-doped porous
multi-nano-channel carbon nanocarbons for use in high-perform-
ance supercapacitor applications. ACS Sustain. Chem. Eng.
4(4), 2439–2448 (2016). https://doi.org/10.1021/acssuc.
hemeng.6b00289

124. Y. Chen, Z. Lu, L. Zhou, Y.W. Mai, H. Huang, Triple-coax-
ial electrospun amorphous carbon nanotubes with hollow
graphitic carbon nanospheres for high-performance Li ion
batteries. Energy Environ. Sci. 5(7), 7898–7902 (2012).
https://doi.org/10.1039/C2EE22085G

125. P. Yang, X. Pan, J. Wang, R. Yang, J. Chu et al., Nozzle-less
 electrospun nitrogen-doped hollow carbon nanofibers as
enhanced sensing platform for carbendazim electrochemical
detection. ChemistrySelect 4(7), 2059–2063 (2019).
https://doi.org/10.1002/slct.201803056

126. Y. Chen, X. Li, K. Park, W. Lu, C. Wang et al., Nitrogen-
doped carbon for sodium-ion battery anode by self-etching
and graphitization of bimetallic MOF-based composite.
Chem 3(1), 152–163 (2017). https://doi.org/10.1016/j.
chempr.2017.05.021

127. Y. Chen, X. Li, K. Park, J. Song, J. Hong et al., Hollow
carbon-nanotube/carbon-nanofiber hybrid anodes for Li-ion
batteries. J. Am. Chem. Soc. 135(44), 16280–16283 (2013).
https://doi.org/10.1021/ja408421n

128. K. Huo, W. An, J. Fu, B. Gao, L. Wang et al., Mesoporous
nitrogen-doped carbon hollow spheres for high-perfor-
manence anodes for lithium-ion batteries. J. Power Sources
324, 233–238 (2016). https://doi.org/10.1016/j.jpows.
our.2016.05.084

129. Q. Chen, G. Ping, X. Zhang, R. Zhao, Q. Wu et al., Nitrogen-
doped mesoporous hollow carbon nanoflowers as high per-
formance anode materials of lithium ion batteries. RSC Adv.
6(96), 93519–93524 (2016). https://doi.org/10.1039/C6RA
1011B

130. C.P. Xu, D.C. Niu, N. Zheng, H.N. Yu, J.P. He et al., Fac-
ile synthesis of nitrogen-doped double-shelled hollow
mesoporous carbon nanospheres as high-performance anode
materials for lithium ion batteries. ACS Sustain. Chem. Eng.
6(5), 5999–6007 (2018). https://doi.org/10.1021/acssuc.
hemeng.7b04617

131. X.Y. Yue, W. Sun, J. Zhang, F. Wang, Y.X. Yang et al.,
Macro-mesoporous hollow carbon spheres as anodes for lithi-
um-ion batteries with high rate capability and excellent
cycling performance. J. Power Sources 331, 10–15 (2016).
https://doi.org/10.1016/j.jpowsour.2016.09.029

© The authors
132. K. Tang, R.J. White, X.K. Mu, M.M. Titirici, P.A. van Aken et al., Hollow carbon nanospheres with a high rate capability for lithium-based batteries. ChemSusChem 5(2), 400–403 (2012). https://doi.org/10.1002/cssc.201100609

133. Z. Sun, X.F. Song, P. Zhang, L. Gao, Template-assisted synthesis of multi-shelled carbon hollow spheres with an ultralarge pore volume as anode materials in Li-ion batteries. RSC Adv. 5(5), 3657–3664 (2015). https://doi.org/10.1039/c4ra10591e

134. L. Song, S. Xin, D.W. Xu, H.Q. Li, H.P. Cong et al., Graphene-wrapped graphitic carbon hollow spheres: bioinspired synthesis and applications in batteries and supercapacitors. ChemNanoMat 2(6), 540–546 (2016). https://doi.org/10.1002/cnma.201600079

135. Y.Q. Zhang, Q. Ma, S.L. Wang, X. Liu, L. Li, Poly(vinyl alcohol)-assisted fabrication of hollow carbon spheres/ reduced graphene oxide nanocomposites for high-performance lithium-ion battery anodes. ACS Nano 12(5), 4824–4834 (2018). https://doi.org/10.1021/acsnano.8b01549

136. J.H. Zhu, Y.P. Wu, X.K. Huang, L. Huang, M.Y. Cao et al., Self-healing liquid metal nanoparticles encapsulated in hollow carbon fibers as a free-standing anode for lithium-ion batteries. Nano Energy 62, 883–889 (2019). https://doi.org/10.1016/j.nanoen.2019.06.023

137. B.S. Lee, S.B. Son, K.M. Park, W.R. Yu, K.H. Oh et al., Anodic properties of hollow carbon nanofibers for Li-ion battery. J. Power Sources 199, 53–60 (2012). https://doi.org/10.1016/j.jpowsour.2011.10.030

138. J. Jang, H.E. Kim, S. Kang, J.H. Bang, C.S. Lee, Urea-assisted template-less synthesis of heavily nitrogen-doped hollow carbon fibers for the anode material of lithium-ion batteries. New J. Chem. 43(9), 3821–3828 (2019). https://doi.org/10.1039/c8nj05807e

139. Z. Chen, Y. Liu, Y. Zhang, F. Shen, G. Yang et al., Ultrafine layered graphene as an anode material for lithium ion batteries. Mater. Lett. 229, 134–137 (2018). https://doi.org/10.1016/j.matlet.2018.06.104

140. F. Xiao, X. Chen, J. Zhang, C. Huang, T. Hu et al., Large-scale production of hollow graphene as high-rate anode for lithium ion batteries. J. Energy Chem. 48, 122–127 (2020). https://doi.org/10.1016/j.jenergychem.2019.12.026

141. S. Heng, X. Shan, W. Wang, Y. Wang, G. Zhu et al., Controllable solid electrolyte interphase precursor for stabilizing natural graphite anode in lithium ion batteries. Carbon 159, 390–400 (2020). https://doi.org/10.1016/j.carbon.2019.12.054

142. D.S. Bin, Y.M. Li, Y.G. Sun, S.Y. Duan, Y.X. Lu et al., Structural engineering of multishelled hollow carbon nanostructures for high-performance Na-ion battery anode. Adv. Energy Mater. 8(26), 1800855 (2018). https://doi.org/10.1002/aenm.201800855

143. K. Tang, L.J. Fu, R.J. White, L.H. Yu, M.M. Titirici et al., Hollow carbon nanospheres with superior rate capability for sodium-based batteries. Adv. Energy Mater. 2(7), 873–877 (2012). https://doi.org/10.1002/aenm.201100691

144. L. Liu, Q.Y. Li, Z.J. Wang, Y. Chen, Phosphorus-doped hollow carbon sphere derived from phytic acid for superior sodium-ion batteries. Mater. Technol. 33(11), 748–753 (2018). https://doi.org/10.1080/10667857.2018.1500131

145. J.C. Ye, J. Zang, Z.W. Tian, M.S. Zheng, Q.F. Dong, Sulfur and nitrogen co-doped hollow carbon spheres for sodium-ion batteries with superior cyclic and rate performance. J. Mater. Chem. A 4(34), 13223–13227 (2016). https://doi.org/10.1039/c6ta04592h

146. Y.H. Qu, Z. Zhang, K. Du, W. Chen, Y.Q. Lai et al., Synthesis of nitrogen-containing hollow carbon microspheres by a modified template method as anodes for advanced sodium batteries. Carbon 105, 103–112 (2016). https://doi.org/10.1016/j.carbon.2016.04.029

147. Y.L. Cao, L.F. Xiao, M.L. Sushko, W. Wang, B. Schwenzer et al., Sodium ion insertion in hollow carbon nanowires for battery applications. Nano Lett. 12(7), 3783–3787 (2012). https://doi.org/10.1021/nl3016957

148. H.X. Han, X.Y. Chen, J.F. Qian, F.P. Zhong, X.M. Feng et al., Hollow carbon nanofibers as high-performance anode materials for sodium-ion batteries. Nanoscale 11(45), 21999–22005 (2019). https://doi.org/10.1039/c9nr07675a

149. Z.G. Luo, S.N. Liu, Y.S. Cai, S. Li, A.Q. Pan et al., Nitrogen/sulfur co-doped hollow carbon nanofiber anode obtained from polypyrrole with enhanced electrochemical performance for Na-ion batteries. Sci. Bull. 63(2), 126–132 (2018). https://doi.org/10.1016/j.scib.2017.12.024

150. H.C. Tao, L.Y. Xiong, S.L. Du, Y.Q. Zhang, X.L. Yang et al., Interwoven n and p dual-doped hollow carbon fibers/graphitic carbon nitride: an ultrahigh capacity and rate anode for Li and Na ion batteries. Carbon 122, 54–63 (2017). https://doi.org/10.1016/j.carbon.2016.06.040

151. W.P. Shi, Y.M. Zhang, Z.Q. Tian, Z.Y. Pan, J.L. Key et al., Low temperature synthesis of polyhedral hollow porous carbon with high rate capability and long-term cycling stability as Li-ion and Na-ion battery anode material. J. Power Sources 398, 149–158 (2018). https://doi.org/10.1016/j.jpowsour.2018.07.038

152. W.B. Li, J.F. Huang, L.L. Cao, Y.J. Ren et al., Controlled synthesis of macroscopic three-dimensional hollow reticulate hard carbon as long-life anode materials for Na-ion batteries. J. Alloys Compd. 716, 210–219 (2017). https://doi.org/10.1016/j.jallcom.2017.05.062

153. N. Sun, H. Liu, B. Xu, Facile synthesis of high performance hard carbon anode materials for sodium ion batteries. J. Mater. Chem. A 3(41), 20560–20566 (2015). https://doi.org/10.1039/C5TA05115E

154. A. Saha, T. Sharabani, E. Evenstein, G.D. Nessim, M. Noked et al., Probing electrochemical behaviour of lignocellulosic, orange peel derived hard carbon as anode for sodium ion battery. J. Electrochem. Soc. 167(9), 090505 (2020). https://doi.org/10.1149/1457-1111/ab7c55

155. Z. Li, Y. Chen, Z. Jian, H. Jiang, J.J. Razink et al., Defective hard carbon anode for Na-ion batteries. Chem. Mater. 30(14), 4536–4542 (2018). https://doi.org/10.1021/acs.chemmater.8b00645

156. J. Ding, H.L. Zhang, H. Zhou, J. Feng, X.R. Zheng et al., Sulfur-grafted hollow carbon spheres for potassium-ion...
battery anodes. Adv. Mater. 31(30), 1900429 (2019). https://doi.org/10.1002/adma.201900429

157. G. Wang, X.H. Xiong, D. Xie, Z.H. Lin, J. Zheng et al., Chemically activated hollow carbon nanospheres as a high-performance anode material for potassium ion batteries. J. Mater. Chem. A 6(47), 24317–24323 (2018). https://doi.org/10.1039/c8ta09751h

158. J.F. Ruan, X. Wu, Y. Wang, S.Y. Zheng, D.L. Sun et al., Nitrogen-doped hollow carbon nanospheres towards the application of potassium ion storage. J. Mater. Chem. A 7(33), 19305–19315 (2019). https://doi.org/10.1039/c9ta05205d

159. D.S. Bin, X.J. Lin, Y.G. Sun, Y.S. Xu, K. Zhang et al., Engineering hollow carbon architecture for high-performance K-ion battery anode. J. Am. Chem. Soc. 140(23), 7127–7134 (2018). https://doi.org/10.1021/jacs.8b02178

160. Z.L. Zhang, B.R. Jia, L. Liu, Y.Z. Zhao, H.Y. Wu et al., Hollow multihole carbon bowls: a stress-release structure design for high-stability and high-volumetric-capacity potassium-ion batteries. ACS Nano 13(10), 11363–11371 (2019). https://doi.org/10.1021/acsnano.9b04728

161. X.P. Wang, K. Han, D.D. Qin, Q. Li, C.Y. Wang et al., Polycrystalline soft carbon semi-hollow microrods as anode for advanced K-ion full batteries. Nanoscale 9(46), 18216–18222 (2017). https://doi.org/10.1039/c7nr06645g

162. Z. Jian, W. Luo, X. Ji, Carbon electrodes for K-ion batteries. J. Am. Chem. Soc. 137(36), 11566–11569 (2015). https://doi.org/10.1021/jacs.5b06809

163. X. Niu, L. Li, J. Qiu, J. Yang, J. Huang et al., Salt-concentrated electrolytes for graphite anode in potassium ion battery. Solid State Ionics 341, 115050 (2019). https://doi.org/10.1016/j.ssi.2019.115050

164. L. Wang, J. Yang, J. Li, T. Chen, S. Chen et al., Graphite as a potassium ion battery anode in carbonate-based electrolyte and ether-based electrolyte. J. Power Sources 409, 24–30 (2019). https://doi.org/10.1016/j.jpowsour.2018.10.092

165. Z.L. Li, Z.B. Xiao, S.Q. Wang, Z.B. Cheng, P.Y. Li et al., Engineered interfusion of hollow nitrogen-doped carbon nanospheres for improving electrochemical behavior and energy density of lithium-sulfur batteries. Adv. Funct. Mater. 29(31), 1902322 (2019). https://doi.org/10.1002/adfm.201902322

166. Y.J. Zhong, Q. Lu, Y.P. Zhu, Y.L. Zhu, W. Zhou et al., Fructose-derived hollow carbon nanospheres with ultrathin and ordered mesoporous shells as cathodes in lithium-sulfur batteries for fast energy storage. Adv. Sustain. Syst. 1(8), 1700081 (2017). https://doi.org/10.1002/adsu.201700081

167. Z. Zhang, G.C. Wang, Y.Q. Lai, J. Li, Z.Y. Zhang et al., Nitrogen-doped porous hollow carbon sphere-decorated separators for advanced lithium-sulfur batteries. J. Power Sources 300, 157–163 (2015). https://doi.org/10.1016/j.jpowsour.2015.09.067

168. D.H. Yang, H.Y. Zhou, H. Liu, B.H. Han, Hollow N-doped carbon polyhedrons with hierarchically porous shell for confinement of polysulfides in lithium-sulfur batteries. Science 13, 243–253 (2019). https://doi.org/10.1016/j.sciset.2019.02.019

169. G.Y. Zheng, Q.F. Zhang, J.J. Cha, Y. Yang, W.Y. Li et al., Amphiphilic surface modification of hollow carbon nanofibers for improved cycle life of lithium-sulfur batteries. Nano Lett. 13(3), 1265–1270 (2013). https://doi.org/10.1021/nl304795g

170. X.Q. Zhang, B. He, W.C. Li, A.H. Lu, Hollow carbon nanofibers with dynamic adjustable pore sizes and closed ends as hosts for high-rate lithium-sulfur battery cathodes. Nano Res. 11(3), 1238–1246 (2018). https://doi.org/10.1007/s12274-017-1737-6

171. G.Y. Zheng, Y. Yang, J.J. Cha, S.S. Hong, Y. Cui, Hollow carbon nanofiber-encapsulated sulfur cathodes for high specific capacity rechargeable lithium batteries. Nano Lett. 11(10), 4462–4467 (2011). https://doi.org/10.1021/nl2027684

172. D. Yang, W. Ni, J.L. Cheng, Z.P. Wang, T. Wang et al., Flexible three-dimensional electrodes of hollow carbon bead strings as graded sulfur reservoirs and the synergistic mechanism for lithium-sulfur batteries. Appl. Surf. Sci. 413, 209–218 (2017). https://doi.org/10.1016/j.apsusc.2017.04.046

173. S.Q. Chen, X.D. Huang, H. Liu, B. Sun, W.K. Yeoh et al., 3D hyperbranched hollow carbon nanorod architectures for high-performance lithium-sulfur batteries. Adv. Energy Mater. 4(8), 1301761 (2014). https://doi.org/10.1002/aenm.201301761

174. F. Pei, T.H. An, J. Zang, X.J. Zhao, X.L. Fang et al., From hollow carbon spheres to n-doped hollow porous carbon bowls: rational design of hollow carbon host for Li-S batteries. Adv. Energy Mater. 6(8), 2502539 (2016). https://doi.org/10.1002/aenm.201502539

175. Y.B. An, Q.Z. Zhu, L.F. Hu, S.K. Yu, Q. Zhao et al., A hollow carbon foam with ultra-high sulfur loading for an integrated cathode of lithium-sulfur batteries. J. Mater. Chem. A 4(40), 15605–15611 (2016). https://doi.org/10.1039/c6ta06088a

176. M. Li, Y.N. Zhang, X.L. Wang, W. Ahn, G.P. Jiang et al., Gas pickering emulsion templated hollow carbon for high rate performance lithium-sulfur batteries. Adv. Funct. Mater. 26(46), 8408–8417 (2016). https://doi.org/10.1002/adfm.201603241

177. C.L. Ma, J. Dong, Y. Zhao, J. Li, H.L. Chen, Dual-template synthesis of novel pomegranate-like hollow carbon nanoparticles with improved electrochemical performance for Li-ion batteries. Carbon 110, 180–188 (2016). https://doi.org/10.1016/j.carbon.2016.09.020

178. J. Zang, J.C. Ye, X.L. Fang, X.W. Zhang, M.S. Zheng et al., Hollow-in-hollow carbon spheres for lithium-ion batteries with superior capacity and cyclic performance. Electrochim. Acta 186, 436–441 (2015). https://doi.org/10.1016/j.electacta.2015.11.002

179. B.S. Lee, S.B. Son, K.M. Park, G. Lee, K.H. Oh et al., Effect of pores in hollow carbon nanofibers on their negative electrode properties for a lithium rechargeable battery. ACS Appl. Mater. Interfaces. 4(12), 6701–6709 (2012). https://doi.org/10.1021/am301873d

© The authors https://doi.org/10.1007/s40820-020-00521-2
180. Z.Y. Pan, H. Sun, J. Pan, J. Zhang, B.J. Wang et al., The creation of hollow walls in carbon nanotubes for high-performance lithium ion batteries. Carbon 133, 384–389 (2018). https://doi.org/10.1016/j.carbon.2018.03.021

181. Q.L. Huang, S.L. Wang, Y. Zhang, B.W. Yu, L.Z. Hou et al., Hollow carbon nanospheres with extremely small size as anode material in lithium-ion batteries with outstanding cycling stability. J. Phys. Chem. C 120(6), 3139–3144 (2016). https://doi.org/10.1021/acs.jpcc.5b10455

182. S.G. Liu, C.P. Mao, L. Wang, M. Jia, Q.Q. Sun et al., Bio-inspired synthesis of carbon hollow microspheres from Aspergillus flavus conidia for lithium-ion batteries. RSC Adv. 5(73), 59655–59658 (2015). https://doi.org/10.1039/c5ra12059d

183. X.H. Dai, H.X. Fan, J.J. Zhang, S.J. Yuan, Sewage sludge-derived porous hollow carbon nanospheres as high-performance anode material for lithium batteries. Electrochim. Acta 319, 277–285 (2019). https://doi.org/10.1016/j.electacta.2019.07.006

184. Q.Q. Li, K. Yao, G.C. Zhang, J. Gong, E. Mijowska et al., Controllable synthesis of 3d hollow-carbon-spheres/graphene-flake hybrid nanostructures from polymer nanocomposite by self-assembly and feasibility for lithium-ion batteries. Part. Part. Syst. Charact. 32(9), 874–879 (2015). https://doi.org/10.1002/ppsc.201500037

185. F.D. Han, Y.J. Bai, R. Liu, B. Yao, Y.X. Qi et al., Template-free synthesis of interconnected hollow carbon nanospheres for high-performance anode material in lithium-ion batteries. Adv. Energy Mater. 1(5), 798–801 (2011). https://doi.org/10.1002/aenm.20100340

186. P. Nie, Z.Y. Le, G. Chen, D. Liu, X.Y. Liu et al., Graphene caging silicon particles for high-performance lithium-ion batteries. Small 14(25), 1800635 (2018). https://doi.org/10.1002/smll.201800635

187. S.M. Zou, X.Y. Xu, Y.Q. Zhu, C.B. Cao, Microwave-assisted preparation of hollow porous carbon spheres and as anode of lithium-ion batteries. Microporous Mesoporous Mater. 251, 114–121 (2017). https://doi.org/10.1016/j.micros.2017.05.062

188. Y.F. Wen, B. Wang, B. Luo, L.Z. Wang, Long-term cycling performance of nitrogen-doped hollow carbon nanospheres as anode materials for sodium-ion batteries. Eur. J. Inorg. Chem. 13–14, 2051–2055 (2016). https://doi.org/10.1002/ejic.201501172

189. K.L. Zhang, X.N. Li, J.W. Liang, Y.C. Zhu, L. Hu et al., Nitrogen-doped porous interconnected double-shelled hollow carbon spheres with high capacity for lithium ion batteries and sodium ion batteries. Electrochim. Acta 155, 174–182 (2015). https://doi.org/10.1016/j.electacta.2014.12.108

190. W.C. Zhang, C.W. Lan, X.H. Xie, Q.Y. Cao, M.T. Zheng et al., Facile construction of hollow carbon nanosphere-interconnected network for advanced sodium-ion battery anode. J. Colloid Interface Sci. 546, 53–59 (2019). https://doi.org/10.1016/j.jcis.2019.03.043

191. Y.H. Qu, Y.M. Deng, Q. Li, Z. Zhang, F.Y. Zeng et al., Core-shell-structured hollow carbon nanofiber@nitrogen-doped porous carbon composite materials as anodes for advanced sodium-ion batteries. J. Mater. Sci. 52(4), 2356–2365 (2017). https://doi.org/10.1007/s10853-016-0528-x

192. J.S. Park, S.Y. Jeong, K.M. Jeon, Y.C. Kang, J.S. Cho, Iron diselenide combined with hollow graphitic carbon nanospheres as a high-performance anode material for sodium-ion batteries. Chem. Eng. J. 339, 97–107 (2018). https://doi.org/10.1016/j.cej.2018.01.118

193. Y.X. Luan, G.D. Nie, X.W. Zhao, N. Qiao, X.C. Liu et al., The integration of sno2 dots and porous carbon nanofibers for flexible supercapacitors. Electrochim. Acta 308, 121–130 (2019). https://doi.org/10.1016/j.electacta.2019.03.204

194. X.W. Zhao, G.D. Nie, Y.X. Luan, X.X. Wang, S.Y. Yan et al., Nitrogen-doped carbon networks derived from the electrospun polyacrylonitrile@branched polyethyleneimine nanofibers as flexible supercapacitor electrodes. J. Alloys Compd. 808, 151737 (2019). https://doi.org/10.1016/j.jallcom.2019.151737

195. S.Z. Zeng, Y.C. Yao, L. Huang, H.L. Wu, B.L. Peng et al., Facile synthesis of ultrahigh-surface-area hollow carbon nanospheres and their application in lithium-sulfur batteries. Chem. Eur. J. 24(8), 1988–1997 (2018). https://doi.org/10.1002/chem.201705211

196. K. Zhang, Q. Zhao, Z.L. Tao, J. Chen, Composite of sulfur impregnated in porous hollow carbon spheres as the cathode of Li-S batteries with high performance. Nano Res. 6(1), 38–46 (2013). https://doi.org/10.1007/s12274-012-0279-1

197. W.D. Zhou, X.C. Xiao, M. Cai, L. Yang, Polydopamine-coated, nitrogen-doped, hollow carbon sulfur double-layered core-shell structure for improving lithium sulfur batteries. Nano Lett. 14(9), 5250–5256 (2014). https://doi.org/10.1021/nl502338b

198. C.F. Zhang, H.B. Wu, C.Z. Yuan, Z.P. Guo, X.W. Lou, Confining sulfur in double-shelled hollow carbon spheres for lithium-sulfur batteries. Angew. Chem. Int. Ed. 51(38), 9592–9595 (2012). https://doi.org/10.1002/anie.201205292

199. W.D. Zhou, C.M. Wang, Q.L. Zhang, H.D. Abruna, Y. He et al., Tailoring pore size of nitrogen-doped hollow carbon nanospheres for confining sulfur in lithium-sulfur batteries. Adv. Energy Mater. 5(16), 1401752 (2015). https://doi.org/10.1002/aenm.201401752

200. X.J. Zhou, J. Tian, Q.P. Wu, J.L. Hu, C.L. Li, N/O dual-doped hollow carbon microspheres constructed by holey nanosheet shells as large-grain cathode host for high loading Li-S batteries. Energy Storage Mater. 24, 644–654 (2020). https://doi.org/10.1016/j.ensm.2019.06.009

201. L. Zhang, B.W. Zhang, Y.H. Dou, Y.X. Wang, M. Al-Mamun et al., Self-assembling hollow carbon nanobeads into double-shell microspheres as a hierarchical sulfur host for sustainable room-temperature sodium sulfur batteries. ACS Appl. Mater. Interfaces 10(24), 20422–20428 (2018). https://doi.org/10.1021/acsami.8b03850

202. Y.J. Zhong, S.F. Wang, Y.J. Sha, M.L. Liu, R. Cai et al., Trapping sulfur in hierarchically porous, hollow indented carbon spheres: a high-performance cathode for lithium-sulfur batteries. J. Power Sources 360, 232–239 (2017). https://doi.org/10.1016/j.jpowsour.2017.02.066
batteries. J. Mater. Chem. A 4(24), 9526–9535 (2016). https://doi.org/10.1039/c6ta03187k

203. Y.P. Xie, L. Fang, H.W. Cheng, C.J. Hu, H.B. Zhao et al., Biological cell derived N-doped hollow porous carbon microspheres for lithium-sulfur batteries. J. Mater. Chem. A 4(40), 15612–15620 (2016). https://doi.org/10.1039/c6ta06164h

204. S.N. Liu, T.Q. Zhao, X.H. Tan, L.M. Guo, J.X. Wu et al., 3D pomegranate-like structures of porous carbon microspheres self-assembled by hollow thin-walled highly-graphitized nanoballs as sulfur immobilizers for Li-S batteries. Nano Energy (2019). https://doi.org/10.1016/j.nanoen.2019.103894

205. N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, Porous hollow carbon@sulfur composites for high-power lithium-sulfur batteries. Angew. Chem. Int. Ed. 50(26), 5904–5908 (2011). https://doi.org/10.1002/anie.201100637

206. G.L. Xia, L.J. Zhang, X.W. Chen, Y.Q. Huang, D.L. Sun et al., Carbon hollow nanobubbles on porous carbon nanofibers: an ideal host for high-performance sodium-sulfur batteries and hydrogen storage. Energy Storage Mater. 14, 314–323 (2018). https://doi.org/10.1016/j.ensm.2018.05.008

207. G. Nie, X. Zhao, Y. Luan, J. Jiang, Z. Kou et al., Key issues facing electrospun carbon nanofibers in energy applications: on-going approaches and challenges. Nanoscale 12, 13225–13248 (2020). https://doi.org/10.1039/D0NR03425H