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ORIGINAL RESEARCH ARTICLE

Preparation and application of carbon-based hollow structured nanomaterials

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ABSTRACT

Carbon-based hollow structured nanomaterials have become one of the hot areas for research and development of hollow structured nanomaterials due to their unique structure, excellent physicochemical properties and promising applications. The design and synthesis of novel carbon-based hollow structured nanomaterials are of great scientific significance and wide application value. The recent research on the synthesis, structure and functionalization of carbon-based hollow structured nanomaterials and their related applications are reviewed. The basic synthetic strategies of carbon-based hollow structure nanomaterials are briefly introduced, and the structural design, material functionalization and main applications of carbon-based hollow structure nanomaterials are described in detail. Finally, the current challenges and opportunities in the synthesis and application of carbon-based hollow structured nanomaterials are discussed.

Keywords: Hollow Structure; Carbon-Based Nanomaterials; Preparation Methods

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1. Introduction

Hollow-structured nanomaterials have been one of the most popular materials among advanced nanomaterials due to their low mass density, high porosity and large surface area. The unique properties of hollow-structured nanomaterials have led to their use in a wide range of applications, such as energy storage and conversion, catalytic, water and air purification and adsorption, etc.[1–4]. In recent years, researchers have focused on the synthesis, characterization and application of hollow structures. Many studies have provided novel insights into the structural and functional design and synthesis of hollow structured nanomaterials, which have contributed to the development of hollow structured nanomaterials[5–8]. Among the many hollow structured nanomaterials, carbon-based hollow structured nanomaterials have attracted much attention due to their great potential applications in energy and catalysis[9].

Carbon-based hollow structured nanomaterials are favored by researchers due to their tunable specific surface area, cavity size, morphological structure and composition. Based on the needs of different applications, the research on carbon-based hollow structure nanomaterials has focused on the design and synthesis of cavity structure, shell structure and functionality. Researchers have focused on obtaining carbon-based hollow structure nanomaterials with the following properties: (1) large specific surface area and effective dispersion and loading of metal nanoparticles or other active substances on their surface, functionalized surface structure; (2) excellent electrical conductivity; (3)

tunable porosity and particle size; and (4) high mechanical stability[10]. In order to impart these excellent properties to carbon materials, a series of synthetic strategies have been successfully developed, such as: Stöber method, template method, microemulsion method, etc.[11–13]. These works have contributed to the development of carbon-based hollow structured nanomaterials and have played an important role in understanding their synthesis mechanisms and expanding their applications.

In this paper, we summarize the basic synthesis strategies of carbon-based hollow structure nanomaterials in terms of synthesis, structure, functionalization design and their related applications in recent years. The structural design and functionalization of carbon-based hollow structured nanomaterials and their main applications are described in detail. The current challenges and opportunities in the synthesis and application of carbon-based hollow structured nanomaterials are discussed.

2. Synthesis and application of carbon-based hollow structured nanomaterials

2.1 Synthesis of carbon-based hollow structured nanomaterials

The synthesis of carbon-based hollow structure nanomaterials is basically the same as the preparation of other hollow structures (**Figure 1**)[9]. It can be divided into hard template method, soft template method and self-template method. The most distinctive feature is that the shell layer is a carbon material. Therefore, the successful coating of carbon precursors on the synthesized templates is the key to the preparation of carbon-based hollow structure nanomaterials. The soft and self-templating methods are relatively limited in the preparation of carbon-based hollow structure nanomaterials. The soft template method usually uses stable surfactant micelles or emulsions as templates, which can only be used for the coating of carbon precursors in the liquid phase system, and the morphology and pore size are relatively difficult to regulate[14]. The self-templating method refers to a template-free strategy, and the preparation of carbon-based hollow structure nanomaterials using this method is generally carbonized with some hollow carbon precursors. In addition, in recent years, some new metal-organic skeletal materials can also be obtained through appropriate control of calcination conditions of carbon-based hollow structure, greatly enriching the scope of self-templating method for the preparation of carbon-based hollow structure nanomaterials[15,16].

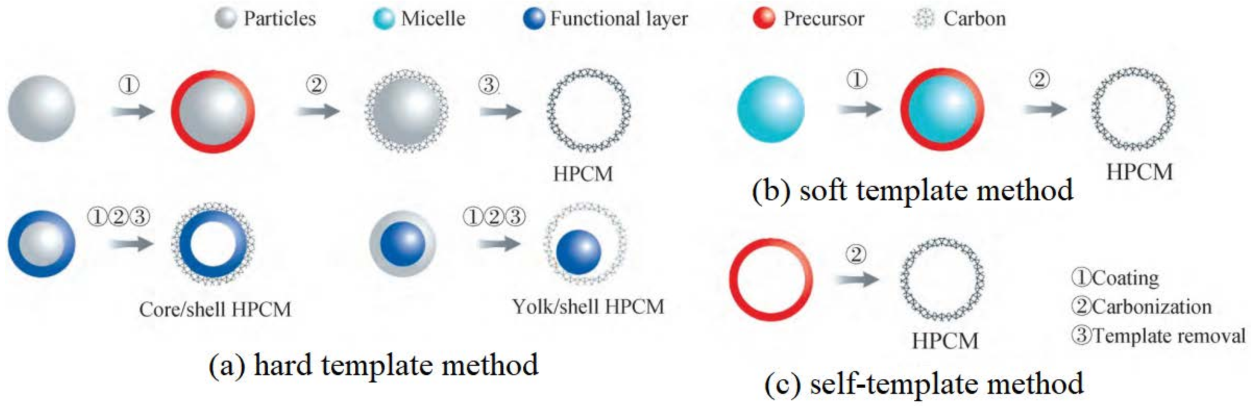

Figure 1. Synthesis of carbon-based hollow nanomaterials[9].

Compared with soft and self-templating methods, hard template method has more advantages in the design and preparation of carbon-based hollow structure nanomaterials, and in consideration of the price and ease of operation, hard templates such as silica, metal oxides and polymers are often chosen. Methane, furfuryl alcohol, glucose, asphalt, and phenolic resins are available as carbon sources. In addition, some nitrogen-containing compounds (e.g., aniline, pyrrole, dopamine, and ionic liquids) have also been used to synthesize heteroatom-doped carbon[17].

The coating strategies of carbon precursors on templates are generally classified into physical and chemical coating. The physical coating is usually performed by vapor deposition (CVD), where the carbon source is usually styrene, acetonitrile, benzene and methane. The main advantage of CVD method is that the thickness of carbon layer can be precisely controlled, especially for depositing atomic layer thickness. However, the size of carbon spheres prepared by this method is mostly limited to larger sizes (>500 nm), and it is difficult to obtain small size hollow carbon spheres by this method. Chen *et al.*[18] used SiO_2@m-SiO_2 with core-shell structure as hard template and ethane as carbon source, and deposited the carbon source into the mesoporous silicon oxide pore channel by CVD method, and then etched the silicon oxide template by hydrofluoric acid to obtain hollow mesoporous carbon material. By controlling the size of the template, the shell thickness and cavity size of the hollow mesoporous carbon spheres were controlled. In addition, the hollow mesoporous carbon spheres were obtained with a high degree of graphitization and a specific surface area of 771 $m^2 \cdot g^{-1}$ due to the use of ethane as the carbon source.

The chemical cladding method uses a chemical reaction to clad the chemical precursors on the outer surface of the template to form a template@carbon precursor core-shell structure complex. Finally, the hollow structure is obtained by etching the template. The development of carbon precursor chemistry is the key to this approach. Considering that the hydrolytic polymerization process and the structure of phenolic resin are similar to the formation of SiO_2. The reaction mechanism is shown in **Figure 2**. Resorcinol and formaldehyde monomers can form emulsion droplets through the interaction of hydrogen bonds in the mixture system of ethanol and water, and then undergo a polymerization reaction catalyzed by ammonia water to form phenolic resin colloidal microspheres. Subsequent studies have shown that this Stöber method can be extended to the hydrolytic polymerization of other carbon precursors, such as phenolic resin derivatives, polydopamine and polybenzoxazine[20,21].

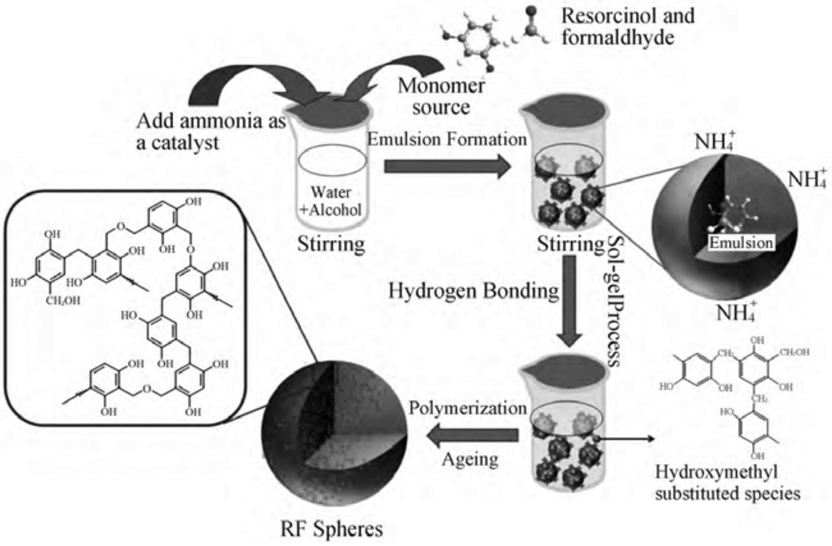

Figure 2. Synthesis of phenolic resin microspheres[19].

Inspired by the successful application of the silicate sol-gel process for the preparation of hollow structured materials, the Stöber method system was also used for the synthesis of carbon-based hollow structured nanomaterials. Using the Stöber system to combine the synthesis of SiO_2 and RF, Fuertes *et al.*[22] synthesized core-shell structured SiO_2@RF microspheres and hollow porous carbon spheres by a one-pot method with TEOS, resorcinol and formaldehyde in a mixture of water, ethanol and ammonia. Yin, Zheng and Huo[23–25] have independently investigated the synthesis of hollow or Yolk-shell structured carbon-based materials by depositing phenolic resin and cationic surfactant complexes on the surface of silicon oxide or silicon oxide core-shell structured nanoparticles. The co-assembly of positively charged cationic surfactants with phenolic resins (RF) on the negatively charged silicon oxide surface is the key to the RF coating process. The introduction of the cationic surfactant enhances the interaction between the two negatively charged materials, RF and the silicon oxide core, allowing the RF to be successfully encapsulated on the surface of the silicon oxide core. In order to further increase the porosity of hollow carbon spheres, Zheng's group[26] developed a multi-step coating process to synthesize a sandwich structure of SiO_2@RF/CTAB@SiO_2 complexes. The hollow carbon spheres obtained with this structure have a foam-like shell, which is similar to that of SiO_2@RF/CTAB-derived hollow carbon spheres (specific surface area and porosity of 639 $m^2 \cdot g^{-1}$ and 0.56 $cm^3 \cdot g^{-1}$, respectively). In comparison, it has a higher specific surface area (1,286 $m^2 \cdot g^{-1}$) and a larger pore volume (2.25 $cm^3 \cdot g^{-1}$). In addition, in the modified Stöber method system, the mechanism of co-assembly of silica-based oligomers, cetyltrimethylammonium chloride (CTAC) and RF, Qiao *et al.* developed a silica-assisted process to regulate the structure and size of pores (**Figure 3**)[27]. The SiO_2@RF/CTAC/SiO_2 composite microspheres were prepared by a one-step reaction using TEOS, formaldehyde and resorcinol in the ethanol/water/ammonia/CTAC system. In the RF/CTAC/SiO_2 composite shell layer, SiO_2 can be used as a pore-forming agent, and the pore size of the hollow carbon sphere shell layer can be adjusted from 3.2 to 3.6 nm when the template is removed. In addition, the size of the hollow spheres (180–800 nm in diameter) can also be adjusted by the amount of TEOS and the water/ethanol ratio.

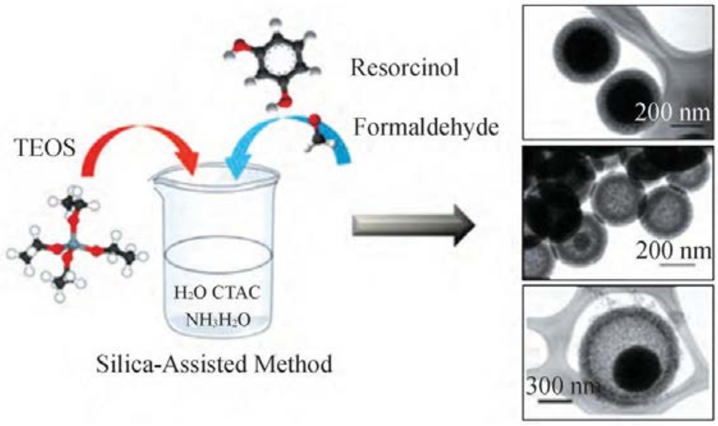

Figure 3. Synthesis of hollow Carbon Nanostructures via a "Silica-Assisted" Strategy[27].

As researchers gained a better understanding of carbon precursor chemistry, they began to work on simplifying the Stöber method for the controlled synthesis of hollow carbon spheres. In recent years, a series of general synthetic methods have been developed for the preparation of hollow carbon spheres, ranging from surfactant-free to silicon oxide free. Wang *et al.*[28] reported a facile synthesis of nitrogen-doped polybenzoxazine microspheres and nitrogen-doped carbon microspheres. The polymer microspheres were obtained by condensation of resorcinol, formaldehyde and 1,6-diaminohexane, and the size could be adjusted by adjusting the temperature parameters. Considering that the positively charged polybenzoxazine can be adsorbed on the negatively charged SiO_2 surface by electrostatic interaction, the nitrogen-doped hollow carbon spheres were further synthesized by the surfactant-free Stöber system designed by Nanfeng Zheng's group. The synthetic route and the resulting products are shown in **Figure 4**. When resorcinol/formaldehyde/ethylenediamine is used as the polybenzoxazine (PB) precursor and TEOS as the SiO_2 precursor, the PB/SiO_2 composite shell layer can be directly coated on the core surface of SiO_2 spheres in a solvent mixture of water and ethanol. In this system, ethylenediamine acts as a base catalyst to promote the hydrolysis of TEOS. The positively charged polybenzoxazine and negatively charged silicon oxide oligomers are coassembled and deposited on the negatively charged SiO_2 core surface to form the SiO_2@PB/SiO_2 core-shell structure. This core-shell structure can be further transformed into nitrogen-doped hollow carbon materials. The structure of hollow carbon spheres can also be changed from a spherical shape to a bowl-shaped hollow structure by changing the ratio of TEOS and PB[29].

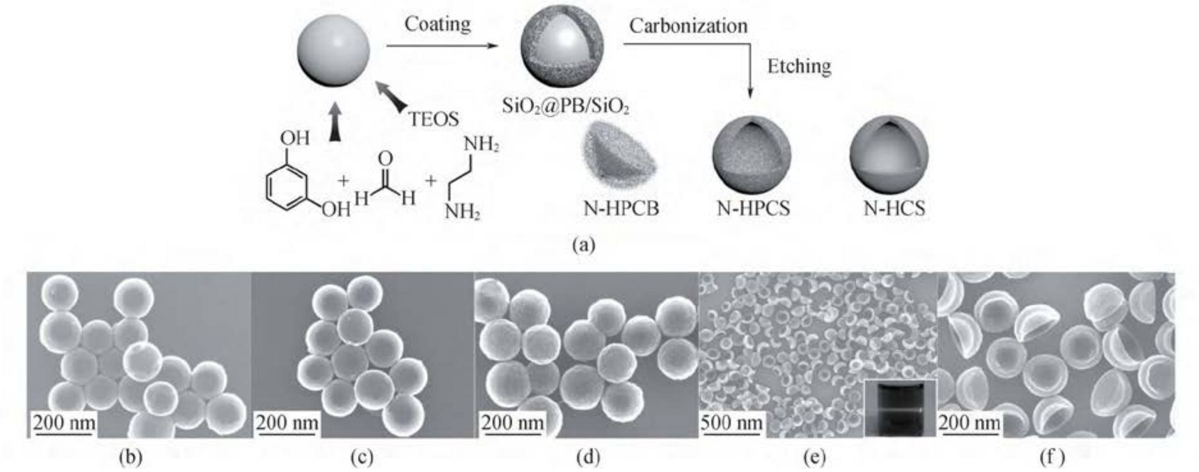

Figure 4. Silica-assisted polybenzoxazine coating strategy for the synthesis of N doped hollow carbon spheres (**a**); SEM images of as-obtained products (**b–f**)[29].

Figure 5. Fabrication of multi-shells hollow carbon spheres using 3-aminophenol/formaldehyde resin[30].

In addition, the hollow carbon spheres were recently prepared by the group of Lijun Wan by selective dissolution of 3-aminophen/formaldehyde resin microspheres (3-AF), which discarded the surfactant and silicon oxide template used in the previous method (**Figure5**)[30]. The polymerization of 3-aminophen and formaldehyde in a mixed system of water and NH_4OH produced 3-aminophen/formaldehyde resin microspheres with a heterogeneous chemical composition. The microspheres are composed of 3-AF oligomers and high molecular weight 3-AF with high polymerization degree, and the overall core-shell structure of oligomers@high polymers. Since the internal oligomer 3-AF can be dissolved by acetone, the prepared 3-aminophenol/formaldehyde resin microspheres can be treated with acetone to obtain hollow 3-AF microspheres. When the hollow 3-AF microspheres were used as a template, the growth and dissolution process was repeated to obtain multishell 3-AF spheres. The corresponding multishell hollow carbon spheres can be obtained by carbonization. This work provides a controlled pathway for the synthesis of multishell hollow carbon spheres. In addition, the Stöber-based strategy for the synthesis of polymeric microspheres has been extended to other polymers in recent years, for example, the successful application of polydopamine provides an effective way to directly prepare nitrogen-doped carbon-based materials[31].

2.2 Morphology and structural design of carbon-based hollow structure nanomaterials

The morphology and structure design of carbon-based hollow nanomaterials are similar to other hollow materials, and the morphology and structure of the templates can be controlled to obtain hollow carbon structures with different morphologies. More importantly, the morphological and functional diversity of carbon-based hollow structure nanomaterials can be enriched through the rational design of template@carbon precursor complexes. When a core/shell material is used as a template,two typical sandwich-like intermediates (e.g., sacrificial layer@functional layer@carbon precursor structure and functional layer@sacrificial layer@carbon precursor structure) can be obtained by coating the template with carbon precursors, which can be converted into hollow core/shell carbon based material and Yolk@Shell hollow carbon based structure after removing the template, respectively. This strategy of modifying hard templates provides an effective way to directly design multifunctional carbon-based functional materials, which greatly facilitates the application of carbon-based hollow structure nanomaterials[32].

Carbon-based hollow structure nanomaterials have great potential for applications in catalysis, drug delivery, and batteries. For these applications, the design of the shell structure is an important aspect to further improve the performance of hollow nanomaterials.

2.2.1 Ultra-thin shell layer design

In carbon-based hollow nanomaterials, the shell structure plays a decisive role in their performance. The thickness of the shell layer directly affects the physicochemical properties of the material, such as electrical conductivity, specific surface area, porosity, density, and the number of active sites available. In energy storage and catalysis applications, nanomaterials with ultra-thin hollow shell layers are preferred by researchers. Liu *et al.* first synthesized SiO_2@PDA core-shell structures under alkaline conditions using dopamine as the green carbon source, and then carbonized and etched the core template to obtain ultra-thin hollow carbon spheres with a shell layer thickness of only 4 nm (**Figure 6**). In addition, Au@C Yolk**-**Shell structure was prepared by using Au@SiO_2 core-shell structure as a template and used in the reduction of nitrobenzene phenol, which showed high catalytic activity and stability[33]. Han *et al.* also developed a template-assisted thermal decomposition method to prepare ultrathin hollow nitrogen-doped carbon spheres loaded with single-atom Co active sites (**Figure 7**)[34], with a shell thickness of 5 nm. The ultrathin carbon shell layer loaded with single-atom Co is beneficial for improving the utilization of active sites. In addition, the ultra-thin shell layer facilitates the transport of the reacting species. The ma terial showed high catalytic activity and stability for oxygen reduction catalytic reactions under acidic conditions.

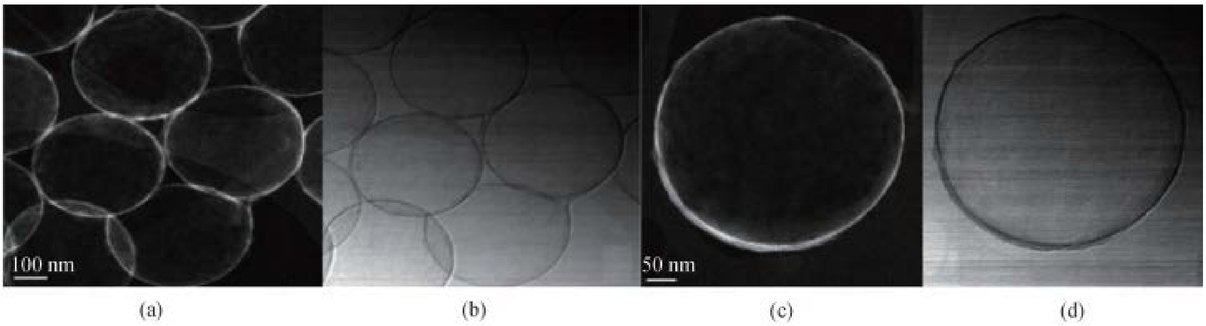

Figure 6. TEM image of super-thin hollow carbon spheres[33].

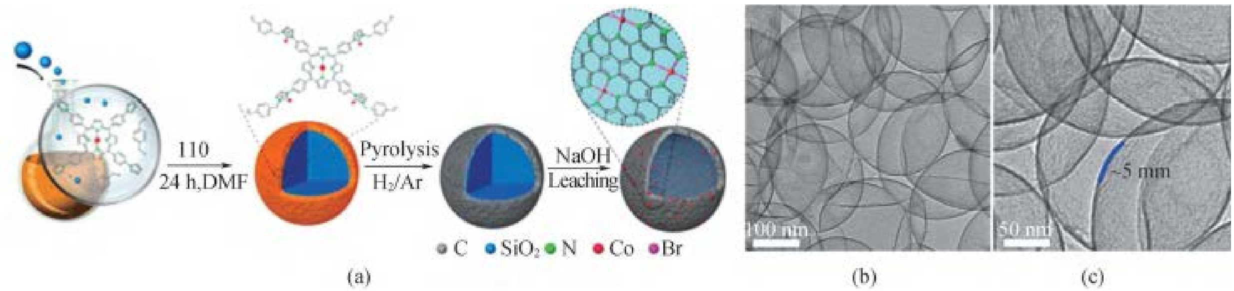

Figure 7. Schematic illustration of the fabrication (**a**) and TEM of images of super-thin hollow carbon spheres (**b**,**c**)[34].

2.2.2 The porous shell layer design

Nanomaterials with porous shell layer structure can further increase the specific surface area of hollow structured materials compared to hollow micro/nano structured materials with solid shell layer. Most of the research in this area is based on a combination of soft and hard template synthesis methods. In addition to the hard template method for cavity fabrication, porogenic agents are introduced during the coating process of the shell layer material, and hollow micro/nano-structured materials with porous shell layer structure can be obtained after the removal of the cavity template and the shell layer porogenic agents[35]. For example, hollow mesoporous carbon microspheres were also successfully synthesized by the co-hydrolysis of organic polymers and inorganic silica-derived precursors by Yu's group at the University of Queensland, Australia[36]. A core-shell structure of phenolic resin/silicon composite shell layer with a silicon oxide core was successfully prepared by co-hydrolysis/cross-linking of resorcinol, formaldehyde and silica in an ethanol/water system, followed by carbonization to remove the template to obtain hollow mesoporous carbon microspheres (**Figure 8**). The final hollow structure and mesoporous shell structure can also be controlled by controlling the amount of silicon source and the type of silicon source in the system. The hollow mesoporous carbon was prepared using a combination of soft and hard templates by Lou from Nanyang Technological University. In the alcohol/water system, the carbon source dopamine, the porogenic agent F127, and the pore expander trimethylbenzene were co-assembled and coated on different substrates catalyzed by ammonia water. After high temperature carbonization, core-shell nanocomposites with mesoporous carbon shell layer were successfully obtained (**Figure 9**). The removal of the substrate template resulted in hollow mesoporous carbon spheres with different morphologies[37].

2.3 Functionalization of carbon-based hollow structured nanomaterials

2.3.1 Heteroatom doping effects

In order to create more active sites and further improve the catalytic activity as well as the interaction between carbon composites and reactants, doping the carbon skeleton with other heteroatoms such as nitrogen (N), boron (B), sulfur (S), phosphorus (P) or a combination has been widely adopted[38]. Among them, the chemical reactivity, electrical conductivity, affinity for CO_2 adsorption and specific capacity for supercapacitors are much better than pure carbon materials due to the introduction of N elements into the carbon skeleton[39,40]. Nitrogen-doped carbon materials can be prepared by: (1) direct carbonization of precursors containing heteroatoms to obtain heteroatom-doped carbon materials; (2) post-processing methods, which refers to the heteroatom post-merging in the pure carbon material skeleton. Usually, the carbon material is calcined together with precursors containing heteroatoms such as ammonia or thiourea. The biggest disadvantage of the post-treatment doping method is that it is difficult for the heteroatoms to enter the carbon skeleton, only a certain modification of the surface carbon atoms is possible. Therefore, most of the efforts have been devoted to the synthesis of homogeneous heteroatom-doped carbon materials using the first approach. To date, significant progress has been made in the design of heteroatom-doped carbon materials based on the molecular level, especially using phenolic resin polymer precursors. A series of nitrogen-containing compounds have been used to prepare nitrogen-doped carbon materials, such as: melamine, aminophenol, 4-amino-3-nitrophenol, 4-aminophenol, hexamethylenetetramine, and 1,6-diaminohexane. In addition, some nitrogen-containing monomers, such as aniline, pyrrole and dopamine, were also used to prepare nitrogen-doped carbon materials. The content of nitrogen in nitrogen-doped carbon materials can be adjusted by regulating the addition of nitrogen-containing precursors and calcination conditions. Similarly, in the preparation of sulfur-doped carbon and boron-doped carbon materials, the corresponding heteroatom-doped carbon materials can be obtained by introducing the corresponding monomers. Polyatomic doped carbon materials can be prepared by introducing monomers containing different elements, or by combining various methods to introduce different elements separately.

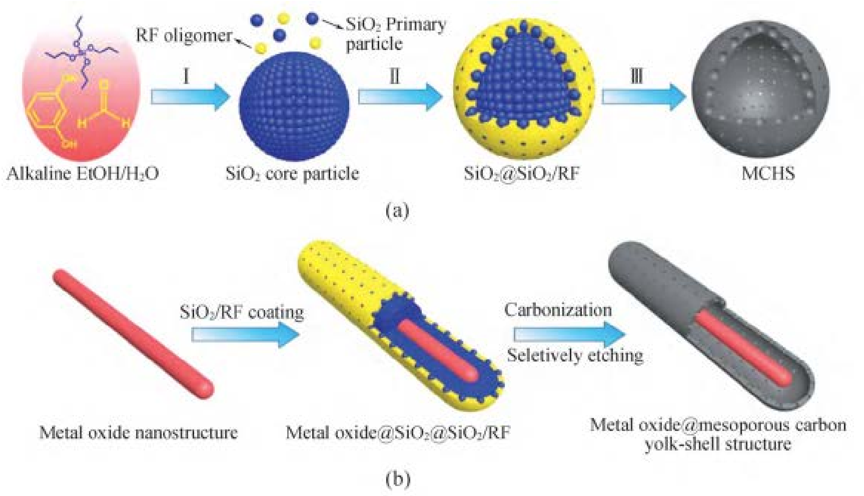

Figure 8. Fabrication of mesoporous carbon structures via a carbon/silica composite shell method[36].

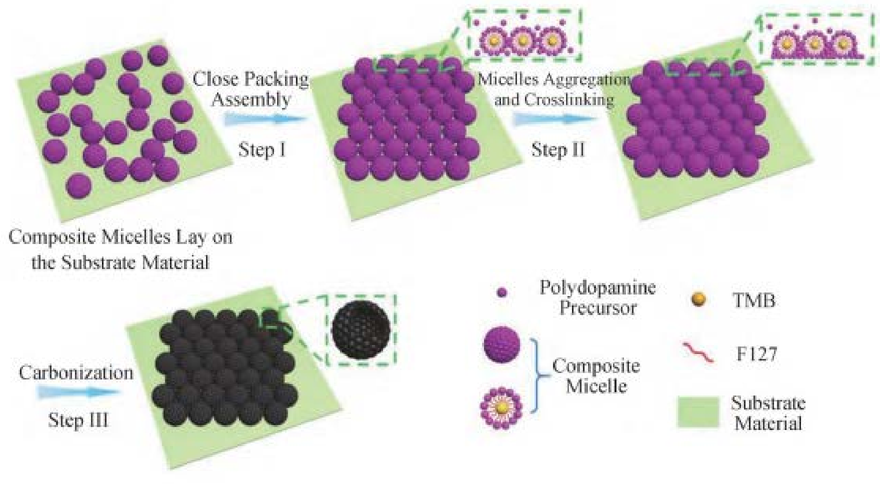

Figure 9. Fabrication of mesoporous carbon spheres via a micelle assembly strategy[37].

2.3.2 Surface modification of carbon materials

Carbon materials are often used as catalyst carriers to enhance the performance of catalytically active materials. Two main approaches can be used to functionalize the surface of carbon: (1) deposition of nanoparticles; (2) surface grafting of functional groups.

The loading of nanoparticles or single atoms on carbon surfaces is often considered an effective way to tune the interfacial properties and improve the molecular interactions to achieve desirable catalytic and electrochemical properties. For nanoparticles highly dispersed on the surface of carbon materials, the size can be adjusted from nanoscale to single atoms, and the smaller the size, the more catalytic sites are exposed, and the corresponding electrochemical and catalytic properties are more desirable. For example, Li's group has successfully loaded highly dispersed cobalt atoms on the surface of hollow nitrogen-doped carbon spheres using a thermal decomposition method. Using this material for oxygen reduction reactions, the atomically dispersed cobalt sites expose the maximum number of catalytic sites, and the hollow structure facilitates the rapid transport of oxygen reduction-related species. This combination of structures gives the material a high catalytic performance[34]. In addition, a similar structure was used to load cobalt atoms in Co-N_5 coordination in nitrogen-doped hollow mesoporous carbon spheres for the CO_2 reduction reaction, which exhibited nearly 100% CO selectivity and high stability[41]. Hollow carbon spheres and carbon-based Yolk-shell structures were considered as ideal carriers to prevent the precipitation and aggregation of noble metals on the surface of carbon carriers at high temperatures in catalytic reactions. Liu *et al.* prepared Ag/AgBr@SiO_2@RF core-shell structure by one-step Stöber method, and obtained Ag@C Yolk-shell nanostructured microspheres by carbon etching the template[42]. In addition, Galeano *et al.* confined small size Pt nanoparticles in mesoporous hollow carbon materials and used them in electrochemical oxygen reduction reactions with much better stability than commercial Pt/C[43,44].

The functional groups on the surface of carbon materials can be used as anchor sites for metal catalysts and contribute to the adsorption of metals on the carbon surface. This usually results in a high dispersion of the metal species on the carbon surface and enhances the chemical properties. Commonly used methods such as oxidation, KOH activation and sulfonation have been widely used for the grafting of functionalized functional groups on the surface of carbon materials[45]. In addition, the polarity of carbon materials can also be changed by the grafting of functional groups, such as the introduction of various polar groups such as carboxyl, nitrate, sulfonic acid and hydroxyl groups on the surface of carbon materials so that its own non-polar surface is transformed into a polar surface. For example, Wang *et al.* obtained sulfonated hollow mesoporous carbon spheres (Ar-SO_3H-HMCS) by etching the core-shell structure of SiO_2@C with hydrofluoric acid and further treatment with chlorosulfonic acid[46].

Song *et al.* successfully synthesized hollow mesoporous carbon spheres functionalized with aryl sulfonic acid by diazo coupling using furfuryl alcohol as the carbon precursor by the hard template method, and the synthetic route is shown in **Figure 10**[47]. The amount of ArSO_3H grafted on the surface of the carbon material could be controlled by the amount of sulfonate. The results showed that the prepared sulfonate-functionalized hollow mesoporous carbon spheres were used as solid acid catalysts with high catalytic activity and stability for the alcoholysis reaction of ethyl levulinate or furfuryl alcohol by esterification of levulinic acid. The strong Brönsted acidity of ArSO_3H**-**HMCSs plays a crucial role in the catalytic activity. The thin carbon shell layer and its hollow structure shorten the diffusion distance of the reacting species and facilitate the rapid transfer between reactants and products.

2.4 Applications of carbon-based hollow structured nanomaterials

2.4.1 Applications in energy storage

For chemical batteries, high cycle stability and multiplicative performance is a goal to be pursued in the design of any type of battery. Fast ion and electron transport requires electrode materials with high conductivity and open structure. High cycling stability requires relatively stable active materials and host electrode materials that can mitigate the large volume expansion of active materials during charging and discharging, or effectively inhibit the dissolution of specific active materials in the electrolyte. Due to their unique structural properties, such as high conductivity, open structure and large cavities, carbon-based hollow structure nanomaterials are widely used to load various battery electrode active materials and relieve the volume expansion of active materials. Hollow carbon spheres can be used as host materials for loading high-capacity but unstable electrode active materials. For example, when silicon is used as the anode material for ba-

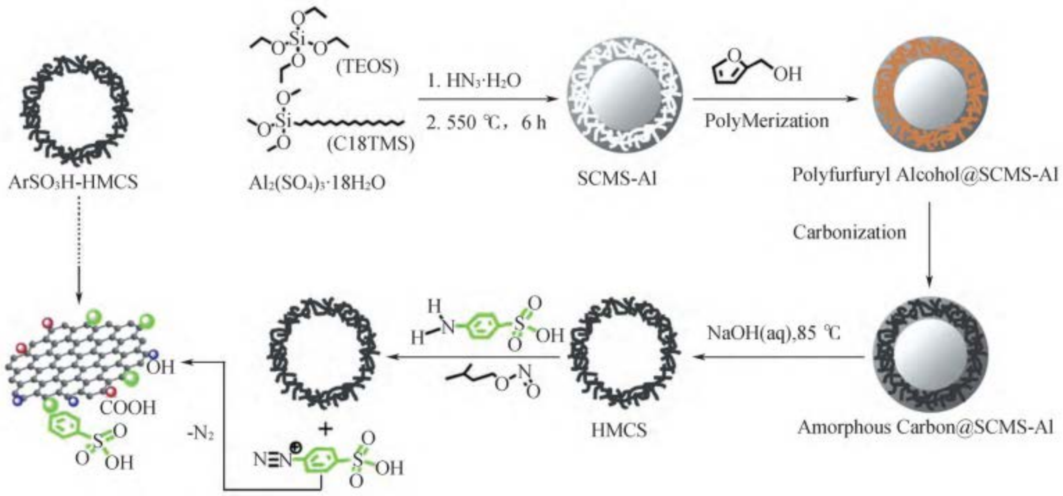

Figure 10. Fabrication of $ArSO_3H$-mesoporous hollow carbon spheres[47].

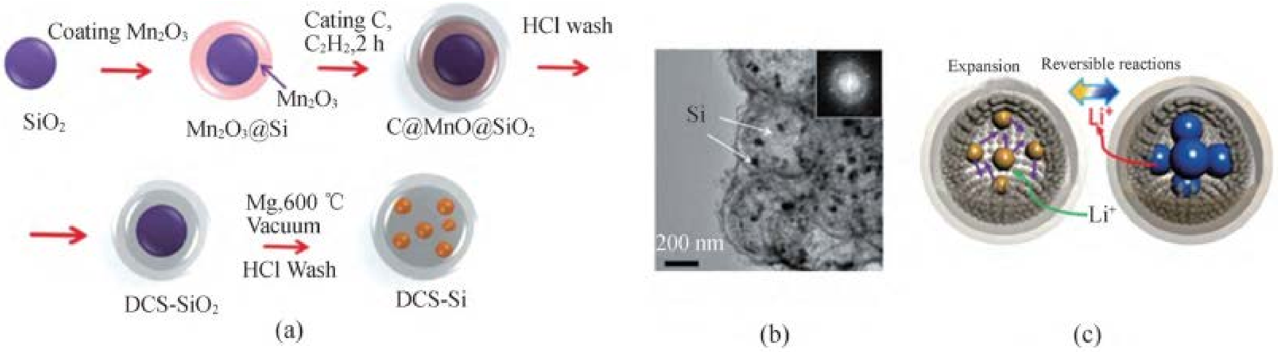

Figure 11. (**a**) Fabrication of silicon nanoparticles confined in double-shell carbon nanoparticles; (**b**) corresponding TEM image of the material, with the selected area electron diffraction (SAED) pattern in the inset; (**c**) structural change of the material during the charge-discharge process[49].

teries, the capacity decays rapidly due to the rupture of the material structure, and the cycling stability is poor[48]. Chen *et al.* confined Si nanoparticles in hollow carbon spheres with a bilayer shell structure by a multi-step coating and etching strategy. The inner carbon shell provides voids to buffer the large volume expansion changes of the Si nanoparticles, while the outer shell helps to form a stable SEI film (**Figure 11**)[49]. Similar strategies have been applied to protect other less stable active materials, such as Sn, SnO_2, MoS_2, etc.[50–52].

Li-S batteries are considered to be one of the most promising secondary batteries due to their high energy density. The cathode active material is non-metallic S. Despite its high theoretical capacity, S has a lot of shortcomings as a battery electrode material. The low electrical conductivity of S, the shuttle effect of lithium polysulfide, and the high-volume expansion limit the practical application of Li-S batteries[53,54]. To alleviate these defects, hollow carbon spheres are widely used as S host materials for Li-S cells. Carbon-based hollow structured nanomaterials loaded with polar inorganic nanoparticles are the most effective strategy to solve the defects of Li-S cells[55–58]. Wu *et al.* used hollow carbon spheres loaded with cobalt oxide nanoparticles (HPCS/CoO) for Li-S batteries, which showed excellent cycling stability[59]. Due to the strong interaction between polar CoO nanoparticles and lithium polysulfide, the shuttle effect phenomenon can be suppressed. Compared with the HPCS/S electrode material, the cycling stability of the HPCS/CoO/S composite electrode material is significantly enhanced, and the capacity can still reach 629 $mAh{\cdot}g^{-1}$ after 1,000 cycles at a current density of 100 C. In contrast, the specific capacity of the HPCS/S electrode after 1,000 cycles is only 302 $mAh{\cdot}g^{-1}$ (**Figure 12**). The researchers also developed C/Co_9S_8, C/TiO, $Fe_3O_4@C$, $MnO_2@HCF$ and other composites for Li-S batteries, which effectively solved the defect problem of S anode and achieved excellent battery performance[60–63].

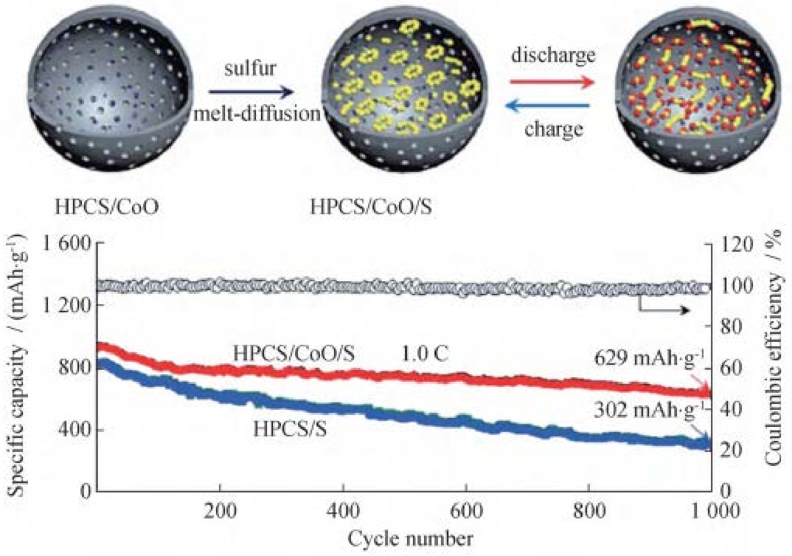

Figure 12. Schematic illustration of the fabrication of HPCS/CoO/S and cycling performanceof HPCS/CoO/S for Li-S battery[59].

Unlike the storage of lithium ions in the battery anode material, lithium metal batteries directly utilize lithium metal as the anode material. Lithium metal has a higher specific capacity (3,860 mAh·g^{-1}) than the conventional graphite anode material used in Li-ion batteries[64]. Very attractive energy densities (e.g., 3,500 Wh·kg^{-1} for Li-O_2 cells and 2,600 Wh·kg^{-1} S cells for Li-S cells) can be obtained when lithium metal cathodes are coupled with other high-capacity cathode materials, such as oxygen and sulfur cathodes[65]. Despite these advantages, lithium metal has inherent defects, including high reactivity, large volume changes during cycling, and formation of lithium dendrites[66]. To solve this problem, surface protection of lithium metal is essential, and hollow carbon microspheres are ideal for solving this problem. The consistent deposition of Li metal in hollow carbon spheres is a great challenge due to the difficulty in controlling its morphology and deposition location during lithium metal deposition. Until recently, Au nanoparticles were first deposited in hollow carbon spheres, and then controlled deposition of Li metal was successfully achieved in hollow carbon spheres using Au as the seed (**Figure 13**). By avoiding direct contact between the lithium metal and the electrolyte,

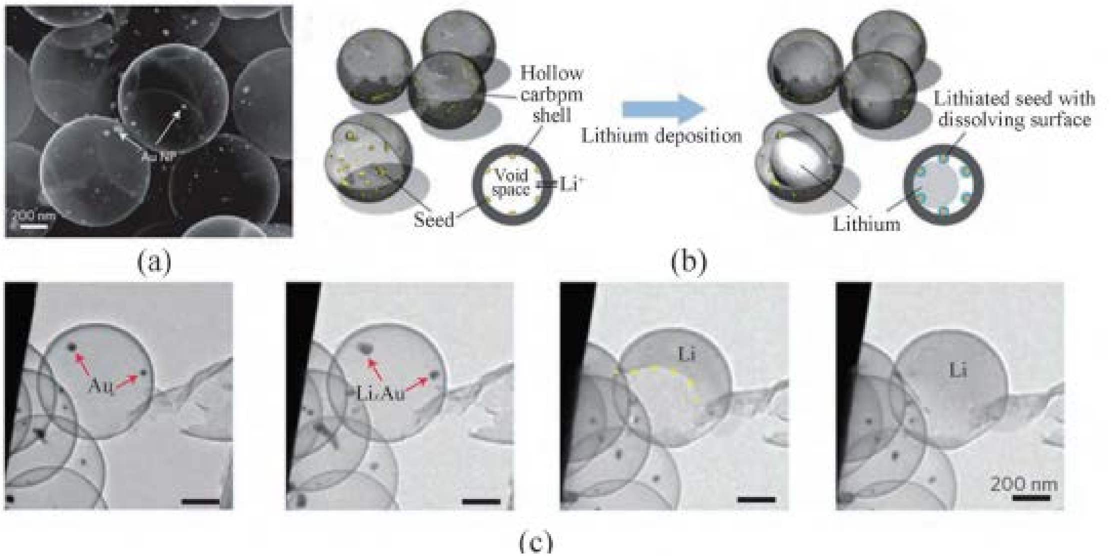

Figure 13. (**a**) TEM images of gold nanoparticles trapped inside hollow carbon nanospheres;(**b**) Lithium deposition process inside the hollow carbon structure;(**c**) Corresponding TEM images of the lithium disposition at different stages[67].

this restricted space can effectively improve the stability of the electrochemical cycle of the lithium metal and minimize the undesirable side effects between the lithium metal and the electrolyte. The cycle performance of the lithium metal cell is improved with a coulombic efficiency of 98% in the carbonate electrolyte and excellent cycle stability over 300 cycles[67].

2.4.2 Applications in electrocatalysis

Electrocatalysis is an important process in the field of clean energy conversion (fuel cells, water splitting and metal-air cells). However, the sluggish kinetics of hydrogen precipitation reactions (HER), oxygen precipitation reactions (OER), and oxygen reduction reactions (ORR) limit the practical applications in these fields. In addition, carbon dioxide reduction, methanol oxidation and nitrogen reduction are also key factors in the conversion of renewable energy sources. Carbon based hollow structured nanomaterials with high electrical conductivity can improve the charge transfer efficiency. In addition, hollow structure and porous structure can improve the mass transfer efficiency. Based on the unique structural characteristics of carbon-based hollow structure nanomaterials mentioned above, researchers generally consider carbon-based hollow structure nanomaterials as one of the best candidates for electrocatalysts with high activity and stability.

The oxygen reduction reaction (ORR) plays a very important role in metal-air cells and fuel cells. Pt electrocatalysts exhibit excellent ORR activity under acidic and alkaline conditions, but their high cost and poor stability have limited the mass production and further practical application of noble metal Pt. In recent years, researchers have focused on the synthesis of low-cost and stable electrocatalysts. Carbon based hollow structured nanomaterials are gaining more and more attention due to their low cost, high activity and stability. Non-metallic carbon-based materials can be doped with various heteroatoms such as N, S and P to modify their electronic structure and chemical activity. The electronegativity and atomic radius differences between heteroatoms and carbon atoms lead to changes in the electronic structure of C atoms adjacent to the heteroatoms, which facilitate the adsorption and electron transfer of oxygen species and enhance their ORR activity. For example, Lou's group developed a strategy to synthesize ultra-thin hollow nitrogen-doped carbon spheres by self-assembling polymer block copolymer F127 and polydopamine composite micelles. The ultrathin shell layer with monolayer mesoporous structure ensured the rapid mass transfer process and high catalytic activity[37]. Although the heteroatom-doped carbon materials exhibited stable and efficient ORR properties in alkaline solutions, their ORR activity under acidic conditions was not satisfactory[68]. To solve this problem, carbon-based materials modified with non-precious metals (Fe, Co, and Ni) have been extensively investigated.

2.4.3 Carbon-based hollow structured nanomaterials as nanoreactors for catalytic reactions

The design of a suitable reactor is essential in chemical reaction engineering. In order to obtain optimal reaction conditions, fluid dynamics, mass transfer, heat transfer, and reaction kinetics must be taken into account. The development of nanotechnology has transformed the reactor vessel from macroscopic to microscopic structures and opened up the concept of new nano-reactors. From the chemical engineering point of view, the designed and prepared catalysts are considered as nano-reactors. Compared to conventional reactors, nanoreactors offer the advantage of parallel chemical reactions, avoiding the formation of undesirable products and enhancing catalytic performance. For example, in hollow carbon-based catalysts, multiple catalytic sites can be located on the inner and outer surfaces of the carbon shell, in the voids of the carbon particles and in anisotropic locations to achieve the best catalytic performance. Compared with solid carbon sphere catalysts, hollow carbon sphere catalytic nano-reactors have the following advantages: (1) catalytically active species can be loaded inside the cavity to prevent the migration and agglomeration of active particles during the catalytic reaction, which leads to the reduction of catalytic activity; (2) selective catalytic activity can be further enhanced by the regulation of shell structure; (3) mass transfer process can be further enhanced during the catalytic reaction compared with the same mass of bulk catalyst; (4) the catalytic reaction rate can be improved by regulating the hydrophilicity/hydrophobicity in the cavity to enrich the reaction products in the cavity[69].

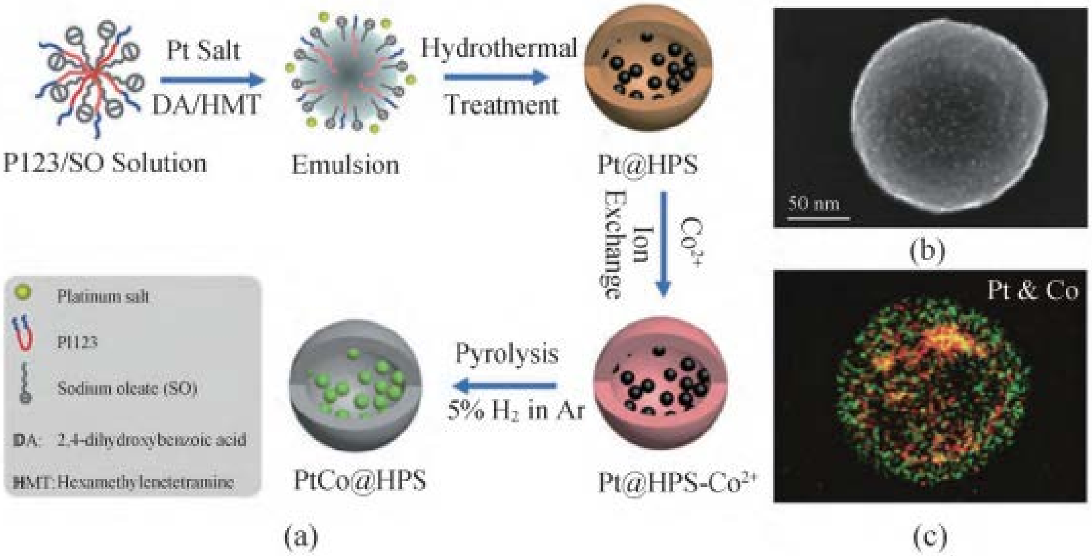

Figure 14. (**a**) Schematic illustration of the synthesis of PtCo@C Yolk-shell micro-spheres; (**b**) TEM image; (**c**) EDX mapping images of PtCo@C Yolk-shell micro-spheres[70].

Selective hydrogenation is essential in organic synthesis, such as the synthesis of epoxy compounds. Most of the catalysis has to be carried out at high temperatures, which makes the active nanoparticles susceptible to sintering and loss of activity during the reaction. Schüth and co-workers developed a simple method to confine 4 nm PtCo nanoparticles inside a hollow carbon sphere cavity (**Figure 14**)[2]. The catalytic conversion of 5-hydroxymethylfurfural to 2,5-dimethylfuran within 10 min was achieved with an efficiency of 100% using this material as a catalyst. The yield of 2,5-furan after 2 h was 98%. In another work, Wang *et al.* successfully prepared Pd@C Yolk-Shell structured catalysts by hydrothermal treatment of emulsions containing P123/sodium oleate/PdCl42- and polymer precursors of 2,4-dihydroxybenzoic acid and hexamethylenetetramine[70]. Recently, Tian *et al.* also reported a Yolk-Shell structured sub-micron reactor loaded with metal nanoparticles in the structure of Pd@Zn/C Yolk-Shell[71]. When used as a catalyst for the hydrogenation of styrene from phenylacetylene, the catalyst achieved 99% selectivity, high conversion and excellent catalytic stability.

3. Conclusions and prospects

In the past decade, carbon-based hollow structured nanomaterials have been developed by leaps and bounds, and fruitful results have been achieved in synthesis, characterization and applications. In this paper, we summarize the basic synthesis strategy, structural design, material functionalization and main applications of carbon-based hollow structured nanomaterials. The unique structure of carbon-based hollow structured nanomaterials has shown great potential applications in many fields.

It is this promising application that the research, development and application of such materials remain a hot topic in the field of hollow structural materials. The future research should focus on the precise regulation of the composition, shell structure and thickness, inner and outer surface properties and loading composition of carbon-based hollow structural materials. To prepare carbon-based hollow structure materials with desired physical properties for different applications. Understanding the conformational relationship between material structure and application properties is the driving force for the development of carbon-based hollow structured nanomaterials and is a major challenge in this field.

Conflict of interest

The authors declared no conflict of interest.

References

1. Liu J, Wickramaratne NP, Qiao S, *et al.* Molecular-based design and emerging applications of nanoporous carbon spheres. Nature Materials 2015; 14(8): 763–774.
2. Wang G, Hilgert J, Richter FH, *et al.* Platinum-cobalt bimetallic nanoparticles in hollow carbon nanospheres for hydrogenolysis of 5-hydroxymethylfurfural. Nature Materials 2014; 13(3): 293–300.
3. Wang X, Feng J, Bai Y, *et al.* Synthesis, properties, and applications of hollow micro-/nanostructures. Chemical Reviews 2016; 116(18): 10983–11060.
4. Xiao M, Wang Z, Lyu M, *et al.* Hollow nanostructures for photocatalysis: Advantages and challenges. Advanced Materials 2019; 31(38): 1801369.
5. Wang J, Cui Y, Wang D. Design of hollow nanostructures for energy storage, conversion and production. Advanced Materials 2019; 31(38): 1801993.
6. Feng J, Yin Y. Self-templating approaches to hollow nanostructures. Advanced Materials 2019; 31(38): 1802349.
7. Mao D, Wan J, Wang J, *et al.* Sequential templating approach: A ground breaking strategy to create hollow multishelled structures. Advanced Materials 2019; 31(38): 1802874.
8. Li H, Yu S. Recent advances on controlled synthesis and engineering of hollow alloyed nanotubes for electrocatalysis. Advanced Materials 2019; 31(38): 1803503.
9. Fu A, Wang C, Pei F, *et al.* Recent advances in hollow porous carbon materials for lithium-sulfur batteries. Small 2019; 15(10): 1804786.
10. Tian H, Liang J, Liu J. Nanoengineering carbon spheres as nanoreactors for sustainable energy applications. Advanced Materials 2019; 31(50): 1903886.
11. Shen Y, Jin J, Chen N, *et al.* Controllable synthesis of porous tubular carbon by a Ag^+-ligand-assisted Stöber-silica/carbon assembly process. Nanoscale 2021; 13(4): 2534–2541.
12. Liu J, Yang T, Wang D, *et al.* A facile soft-template synthesis of mesoporous polymeric and carbonaceous nanospheres. Nature Communications 2013; 4(1): 1–7.
13. White RJ, Tauer K, Antonietti M, *et al.* Functional hollow carbon nanospheres by latex templating. Journal of the American Chemical Society 2010; 132(49): 17360–17363.
14. Xu F, Tang Z, Huang S, *et al.* Facile synthesis of ultrahigh-surface-area hollow carbon nanospheres for enhanced adsorption and energy storage. Nature Communications 2015; 6(1): 7221.
15. Chen T, Zhang Z, Cheng B, *et al.* Self-templated formation of interlaced carbon nanotubes threaded hollow Co_3S_4 nanoboxes for high-rate and heat-resistant lithium-sulfur batteries. Journal of the American Chemical Society 2017; 139(36): 12710–12715.
16. Yao L, Gu Q, Yu X. Three-dimensional MOFs@ MXene Aerogel composite derived MXene threaded hollow carbon confined CoS nanoparticles toward advanced alkali-ion batteries. ACS Nano 2021; 15(2): 3228–3240.
17. Schneider A, Suchomski C, Sommer H, *et al.* Free-standing and binder-free highly N-doped carbon/sulfur cathodes with tailorable loading for high-areal-capacity lithium-sulfur batteries. Journal of Materials Chemistry A 2015; 3(41): 20482–20486.
18. Chen X, Kierzek K, Jiang Z, *et al.* Synthesis, growth mechanism, and electrochemical properties of hollow mesoporous carbon spheres with controlled diameter. The Journal of Physical Chemistry C 2011; 115(36): 17717–17724.
19. Liu J, Qiao S, Liu H, *et al.* Extension of the Stöber method to the preparation of monodisperse resorcinol-formaldehyde resin polymer and carbon spheres. Angewandte Chemie International Edition 2011; 50(26): 5947–5951.
20. Ai K, Liu Y, Ruan C, *et al.* Sp2 C-dominant N-doped carbon sub-micrometer spheres with a tunable size: A versatile platform for highly efficient oxygen-reduction catalysts. Advanced Materials 2013; 25(7): 998–1003.
21. Lu A, Sun T, Li W, *et al.* Synthesis of discrete and dispersible hollow carbon nanospheres with high uniformity by using confined nanospace pyrolysis. Angewandte Chemie International Edition 2011; 50(49): 11765–11768.
22. Noonan O, Zhang H, Song H, *et al.* In situ Stöber templating: Facile synthesis of hollow mesoporous carbon spheres from silica-polymer composites for ultra-high level in-cavity adsorption. Journal of Materials Chemistry A 2016; 4(23): 9063–9071.
23. Li N, Zhang Q, Liu J, *et al.* Sol-gel coating of inorganic nanostructures with resorcinol-formaldehyde resin. Chemical Communications 2013; 49(45): 5135–5137.
24. Fang X, Liu S, Zang J, *et al.* Precisely controlled resorcinol-formaldehyde resin coating for fabricating core-shell, hollow, and yolk-shell carbon nanostructures. Nanoscale 2013; 5(15): 6908–6916.
25. Guan B, Wang X, Xiao Y, *et al.* A versatile cooperative template-directed coating method to construct uniform microporous carbon shells for multifunctional core-shell nanocomposites. Nanoscale 2013; 5(6): 2469–2475.
26. Fang X, Zang J, Wang X, *et al.* A multiple coating route to hollow carbon spheres with foam-like shells and their applications in supercapacitor and confined catalysis. Journal of Materials Chemistry A 2014;

2(17): 6191–6197.

27. Qiao Z, Guo B, Binder AJ, *et al.* Controlled synthesis of mesoporous carbon nanostructures via a “silica-assisted” strategy. Nano Letters 2013; 13(1): 207–212.
28. Wang S, Li W, Hao G, *et al.* Temperature-programmed precise control over the sizes of carbon nanospheres based on benzoxazine chemistry. Journal of the American Chemical Society 2011; 133(39): 15304–15307.
29. Pei F, An T, Zang J, *et al.* From hollow carbon spheres to N-doped hollow porous carbon bowls: Rational design of hollow carbon host for Li-S batteries. Advanced Energy Materials 2016; 6(8): 1502539.
30. Bin D, Chi Z, Li Y, *et al.* Controlling the compositional chemistry in single nanoparticles for functional hollow carbon nanospheres. Journal of the American Chemical Society 2017; 139(38): 13492–13498.
31. Liu C, Wang J, Li J, *et al.* Controllable synthesis of functional hollow carbon nanostructures with dopamine as precursor for supercapacitors. ACS Applied Materials & Interfaces 2015; 7(33): 18609–18617.
32. Liu J, Qiao S, Chen J, *et al.* Yolk/shell nanoparticles: New platforms for nanoreactors, drug delivery and lithium-ion batteries. Chemical Communications 2011; 47(47): 12578–12591.
33. Liu R, Mahurin SM, Li C, *et al.* Dopamine as a carbon source: The controlled synthesis of hollow carbon spheres and yolk-structured carbon nanocomposites. Angewandte Chemie International Edition 2011; 50(30): 6799–6802.
34. Han Y, Wang Y, Chen W, *et al.* Hollow N-doped carbon spheres with isolated cobalt single atomic sites: Superior electrocatalysts for oxygen reduction. Journal of the American Chemical Society 2017; 139(48): 17269–17272.
35. Wan X, Wu H, Guan B, *et al.* Confining sub-nanometer Pt clusters in hollow mesoporous carbon spheres for boosting hydrogen evolution activity. Advanced Materials 2020; 32(7): 1901349.
36. Zhang H, Noonan O, Huang X, *et al.* Surfactant-free assembly of mesoporous carbon hollow spheres with large tunable pore sizes. ACS Nano 2016; 10(4): 4579–4586.
37. Guan B, Yu L, Lou X. Chemically assisted formation of monolayer colloidosomes on functional particles. Advanced Materials 2016; 28(43): 9596–9601.
38. Jiao Y, Zheng Y, Jaroniec M, *et al.* Design of electrocatalysts for oxygen- and hydrogen-involving energy conversion reactions. Chemical Society Reviews 2015; 44(8): 2060–2086.
39. Wickramaratne NP, Xu J, Wang M, *et al.* Nitrogen enriched porous carbon spheres: Attractive materials for supercapacitor electrodes and CO_2 adsorption. Chemistry of Materials 2014; 26(9): 2820–2828.
40. Su F, Poh CK, Chen J, *et al.* Nitrogen-containing microporous carbon nanospheres with improved capacitive properties. Energy & Environmental Science 2011; 4(3): 717–724.
41. Pan Y, Lin R, Chen Y, *et al.* Design of single-atom Co-N_5 catalytic site: A robust electrocatalyst for CO_2 reduction with nearly 100% CO selectivity and remarkable stability. Journal of the American Chemical Society 2018; 140(12): 4218–4221.
42. Liu R, Yeh YW, Tam VH, *et al.* One-pot Stöber route yields template for Ag@ carbon yolk-shell nanostructures. Chemical Communications 2014; 50(65): 9056–9059.
43. Galeano C, Meier JC, Soorholtz M, *et al.* Nitrogen-doped hollow carbon spheres as a support for platinum-based electrocatalysts. ACS Catalysis 2014; 4(11): 3856–3868.
44. Galeano C, Meier JC, Peinecke V, *et al.* Toward highly stable electrocatalysts via nanoparticle pore confinement. Journal of the American Chemical Society 2012; 134(50): 20457–20465.
45. Tang J, Liu J, Torad NL, *et al.* Tailored design of functional nanoporous carbon materials toward fuel cell applications. Nano Today 2014; 9(3): 305–323.
46. Wang L, Zhang J, Yang S, *et al.* Sulfonated hollow sphere carbon as an efficient catalyst for acetalisation of glycerol. Journal of Materials Chemistry A 2013; 1(33): 9422–9426.
47. Song D, An S, Lu B, *et al.* Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate. Applied Catalysis B: Environmental 2015; 179: 445–457.
48. Boukamp BA, Lesh GC, Huggins RA. All-solid lithium electrodes with mixed-conductor matrix. Journal of the Electrochemical Society 1981; 128(4): 725.
49. Chen S, Shen L, van Aken PA, *et al.* Dual-functionalized double carbon shells coated silicon nanoparticles for high performance lithium-ion batteries. Advanced Materials 2017; 29(21): 1605650.
50. Zhang W, Hu J, Guo Y, *et al.* Tin-nanoparticles encapsulated in elastic hollow carbon spheres for high-performance anode material in lithium-Ion batteries. Advanced Materials 2008; 20(6): 1160–1165.
51. Yang T, Liang J, Sultana I, *et al.* Formation of hollow MoS2/carbon microspheres for high capacity and high rate reversible alkali-ion storage. Journal of Materials Chemistry A 2018; 6(18): 8280–8288.
52. An W, Fu J, Su J, *et al.* Mesoporous hollow nanospheres consisting of carbon coated silica nanoparticles for robust lithium-ion battery anodes. Journal of Power Sources 2017; 345: 227–236.
53. Liang J, Sun Z, Li F, *et al.* Carbon materials for Li-S batteries: Functional evolution and performance improvement. Energy Storage Materials 2016; 2: 76–106.
54. Hong X, Mei J, Wen L, *et al.* Nonlithium metal-sulfur batteries: Steps toward a leap. Advanced Materials 2019; 31(5): 1802822.
55. Li L, Chen L, Mukherjee S, *et al.* Phosphorene as a

polysulfide immobilizer and catalyst in high-performance lithium-sulfur batteries. Advanced Materials 2017; 29(2): 1602734.

56. Tao Y, Wei Y, Liu Y, *et al.* Kinetically-enhanced polysulfide redox reactions by Nb_2O_5 nanocrystals for high-rate lithium-sulfur battery. Energy & Environmental Science 2016; 9(10): 3230–3239.
57. Hu L, Dai C, Liu H, *et al.* Double-shelled NiO-$NiCo_2O_4$ heterostructure@ carbon hollow nanocages as an efficient sulfur host for advanced lithium-sulfur batteries. Advanced Energy Materials 2018; 8(23): 1800709.
58. Ye C, Zhang L, Guo C, *et al.* A 3D hybrid of chemically coupled nickel sulfide and hollow carbon spheres for high performance lithium-sulfur batteries. Advanced Functional Materials 2017; 27(33): 1702524.
59. Wu S, Wang Y, Na S, *et al.* Porous hollow carbon nanospheres embedded with well-dispersed cobalt monoxide nanocrystals as effective polysulfide reservoirs for high-rate and long-cycle lithium-sulfur batteries. Journal of Materials Chemistry A 2017; 5(33): 17352–17359.
60. Chen T, Ma L, Cheng B, *et al.* Metallic and polar Co_9S_8 inlaid carbon hollow nanopolyhedra as efficient polysulfide mediator for lithium-sulfur batteries. Nano Energy 2017; 38: 239–248.
61. Li Z, Zhang J, Guan B, *et al.* A sulfur host based on titanium monoxide@ carbon hollow spheres for advanced lithium-sulfur batteries. Nature Communications 2016; 7(1): 13065.
62. Li Z, Zhang J, Lou X. Hollow carbon nanofibers filled with MnO2 nanosheets as efficient sulfur hosts for lithium-sulfur batteries. Angewandte Chemie International Edition 2015; 54(44): 12886–12890.
63. Liang Z, Ma Y, Song J, *et al.* Study on proparation of B/P/N/O Co-doped carbon nanofibers and its pwperties for super capacitors. Journal of Enginnering of Heilongjiang University 2020; 11(2): 38–43.
64. He J, Luo L, Chen Y, *et al.* Yolk-shelled C@ Fe_3O_4 nanoboxes as efficient sulfur hosts for high-performance lithium-sulfur batteries. Advanced Materials 2017; 29(34): 1702707.
65. Ye H, Xin S, Yin Y, *et al.* Advanced porous carbon materials for high-efficient lithium metal anodes. Advanced Energy Materials 2017; 7(23): 1700530.
66. Wang L, Zhou Z, Yan X, *et al.* Engineering of lithium-metal anodes towards a safe and stable battery. Energy Storage Materials 2018; 14: 22–48.
67. Yan K, Lu Z, Lee HW, *et al.* Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. Nature Energy 2016; 1(3): 16010.
68. Yang T, Liu J, Zhou R, *et al.* N-doped mesoporous carbon spheres as the oxygen reduction reaction catalysts. Journal of Materials Chemistry A 2014; 2(42): 18139–18146.
69. Prieto G, Tuüysuüz H, Duyckaerts N, *et al.* Hollow nano- and microstructures as catalysts. Chemical Reviews 2016; 116(22): 14056–14119.
70. Wang G, Chen K, Engelhardt J, *et al.* Scalable one-pot synthesis of yolk-shell carbon nanospheres with yolk-supported Pd nanoparticles for size-selective catalysis. Chemistry of Materials 2018; 30(8): 2483–2487.
71. Tian H, Huang F, Zhu Y, *et al.* The Development of yolk-shell-structured Pd&ZnO@ carbon submicroreactors with high selectivity and stability. Advanced Functional Materials 2018; 28(32): 1801737.