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REVIEW ARTICLE

Synthesis and application of carbon-based hollow nanomaterials

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ABSTRACT

Carbon-based hollow nanomaterials have recently become one of the hot research topics because of their unique structures, outstanding physicochemical properties and potential applications. The design and synthesis of novel carbon-based hollow nanomaterials have important scientific significance and wide application value. The recent researches on designing of synthesis, structure, function and application of carbon-based hollow nanomaterials are reviewed. The common synthesis strategies of carbon-based hollow nanomaterials are briefly introduced. It is described in detail about the structural designing, material functionalization and main applications of carbon-based hollow nanomaterials. At the end of this review, the current challenges as well as opportunities in the synthesis and application of carbon-based hollow nanomaterials are discussed.

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

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1. Introduction

Hollow structure nanomaterials have always been one of the most attractive materials in advanced nanomaterials because of their low mass density, high porosity and large surface area. The unique properties of hollow structure nanomaterials make them widely used in various fields, such as energy storage and conversion catalysis, purification and adsorption of water and air and so on[1–4]. In recent years, researchers have devoted themselves to the synthesis, characterization and application of hollow structures. Many research works have put forward many new ideas on the design and synthesis of the structure and function of hollow structure nanomaterials, which has played a positive role in promoting the development of hollow structure nanomaterials[5–8]. Among many hollow structure nanomaterials, carbon-based hollow structure nanomaterials have attracted much attention because of their great potential application value in the field of energy and catalysis[9].

Carbon-based hollow structure nanomaterials are favored by researchers because of their adjustable specific surface area, cavity size, morphology, structure and composition. Based on the needs of different applications, the research of carbon-based hollow structure nanomaterials mainly focuses on the design and synthesis of cavity structure, shell structure and functionality. Researchers are committed to obtaining carbon-based hollow structure nanomaterials with the following excellent properties: 1) Large specific surface area and effective dispersion and loading of metal nanoparticles or other active substances on its surface to functionalize the surface structure; 2) Excellent conductivity; 3) Adjustable porosity and particle size; 4) High mechanical stability[10]. In order to give these excellent properties to carbon materials, a series of synthetic strategies have been successfully developed, such as Stöber method, template method, microemulsion method and so on[11–13]. These works promote the development of carbon-based hollow structure nanomaterials, and play an important role in a deeper understanding of their synthesis mechanism and expanding related applications.

This paper summarizes the research on the synthesis, structure, functional design and related applications of carbon-based hollow structure nanomaterials in recent years, and the basic synthesis strategies of carbon-based hollow structure nanomaterials. The structural design, material functionalization and main applications of carbon-based hollow structure nanomaterials are described in detail. The challenges and opportunities in the synthesis and application of carbon-based hollow structure nanomaterials are discussed.

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

2.1 Synthesis of carbon-based hollow structure nanomaterials

The synthesis method of carbon-based hollow structure nanomaterials is basically the same as that of other hollow structures (**Figure 1**)[9]. It can be divided into hard template method, soft template method and self-template method. The most remarkable feature is that the shell is made of carbon material. Therefore, the successful coating of carbon precursors on the synthesized template is the key to the preparation of carbon-based hollow structure nanomaterials. The soft template method and self template method have great limitations in the preparation of carbon-based hollow structure nanomaterials. The soft template method usually uses stable surfactant micelles or emulsion as templates, and can only be used to encapsulate carbon precursors in liquid phase. The morphology and pore size of them are relatively difficult to control[14]. Self template method refers to the template free strategy. The preparation of carbon-based hollow structure nanomaterials by this method is generally carbonizing some hollow carbon precursors. In addition, in recent years, some new metal organic framework materials can also obtain carbon-based hollow structures by properly controlling the calcination conditions, which greatly enriches the range of carbon-based hollow structure nanomaterials prepared by self template method[15,16].

Compared with soft template method and self template method, hard template method has more advantages in the design and preparation of carbon-based hollow structure nanomaterials. Considering the price and ease of operation, the common-used hard templates include silica, metal oxide and polymer. Alternative carbon sources include methane, furfuralcohol, glucose, asphalt and phenolic resin. In addition, some nitrogen-containing compounds (such

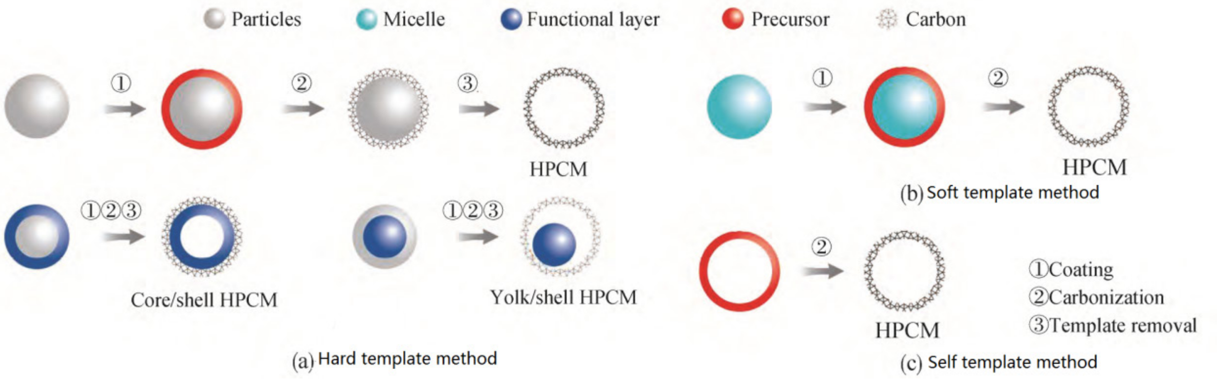

Figure 1. Synthesis of carbon-based hollow nanomaterials[9].

as 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 divided into physical coating and chemical coating. Vapor deposition (CVD) is generally used for physical coating, in which styrene, acetonitrile, benzene and methane are usually used as carbon sources. The greatest advantage of CVD method is that it can accurately control the thickness of carbon layer, especially the carbon layer with atomic layer thickness. However, the size of carbon spheres prepared by this method is mostly limited to large size (>500 nm), and it is difficult to obtain small-size hollow carbon spheres by this method. Chen X *et al.*[18] used SiO_2@ m-SiO_2 with core-shell structure as hard template and ethane as carbon source, deposited the carbon source into mesoporous silica channel by CVD method, and then etched the silica template by hydrofluoric acid to obtain hollow mesoporous carbon material. The shell thickness and cavity size of hollow mesoporous carbon spheres were controlled by controlling the size of the template. In addition, due to the selection of ethane as carbon source, the hollow mesoporous carbon spheres have a high degree of graphitization and a specific surface area of 771 $m^2 \cdot g^{-1}$.

Chemical coating method is to coat the chemical precursor on the outer surface of the template by chemical reaction to form the template@ carbon precursor core-shell structure composite, then calcine the composite in inert gas to convert the carbon precursor into carbon layer, and finally etch the template to obtain hollow structure. The development of carbon precursor chemistry is the key to this method. Considering that the hydrolysis polymerization process and structure of phenolic resin are similar to the formation process of SiO_2. The Qiao Shizhang's group used a similar Stöber method to synthesize resorcinol formaldehyde resin (RF) ball by sol-gel process, and successfully converted it into carbon spheres by calcination[19]. The reaction mechanism is shown in **Figure 2**. Resorcinol and formaldehyde monomer can form emulsion droplets in the mixture of ethanol and water by hydrogen bonding. The phenolic resin colloidal microspheres were formed by polymerization catalyzed by ammonia. Subsequent studies show that this Stöber method can also be extended to the hydrolysis polymerization of other carbon precursors, such as phenolic resin derivatives, polydopamine and polybenzoxazine[20,21].

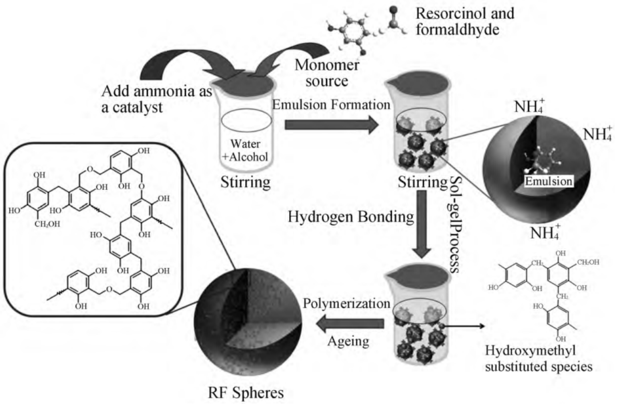

Figure 2. Synthesis of phenolic resin microspheres[19].

Inspired by the successful application of silicate sol-gel process to prepare hollow structural materials, the Stöber system is also used to synthesize carbon-based hollow structural nanomaterials. The synthesis process of SiO_2 and RF was combined by Stöber method. Fuertes *et al.*[22] added TEOS, resorcinol and ormaldehyde into the mixed system of water, ethanol and ammonia to synthesize core-shell SiO_2@ RF microspheres and hollow porous carbon spheres in one pot. Yin Yadong, Zheng Nanfeng and Huo Qisheng *et al.*[23–25] have independently studied the deposition of phenolic resin and cationic surfactant composite coating on the surface of silica or silica core-shell nanoparticles, and the controllable synthesis of carbon-based materials with hollow structure or Yolk-Shell structure. The co-assembly of positively charged cationic surfactant and phenolic resin (RF) on negatively charged silica surface is the key in the process of RF coating. The introduction of cationic surfactant enhances the interaction between two negatively charged materials RF and silicon oxide core, so that RF can be successfully coated on the surface of silicon oxide core. In order to further increase the porosity of hollow carbon spheres, Zheng Nanfeng[26] developed a multi-step coating process to synthesize sandwich structure SiO_2@ RF/CTAB@ SiO_2 composites. The hollow carbon sphere shell obtained by this structure is foamed, compared with the hollow carbon spheres derived from SiO_2 RF/CTAB (specific surface area and porosity respectively 639 $m^2 \cdot g^{-1}$ and 0.56 $cm^3 \cdot g^{-1}$). It has higher specific surface area (1,286 $m^2 \cdot g^{-1}$) and larger pore volume (2.25 $cm^3 \cdot g^{-1}$). In addition, based on the mechanism of CO assembly of cetyltrimethylammonium chloride (CTAC) and RF, Qiao Z A *et al.* developed a silicon oxide assisted process to regulate the structure and size of pores (**Figure 3**) [27]. SiO_2@ RF/CTAC/SiO_2 composite microspheres were prepared by one-step reaction of TEOS, formaldehyde and resorcinol in ethanol/water/ammonia/CTAC system. In RF/CTAC/SiO_2 composite shell, SiO_2 can be used as pore forming agent, and the pore diameter of carbon spherical shell can be adjusted in 3.2 ~ 3.6 nm when removing the template. In addition, the size of the hollow sphere (180 to 800 nm in diameter) can also be regulated by the amount of TEOS as well as the water/ethanol ratio.

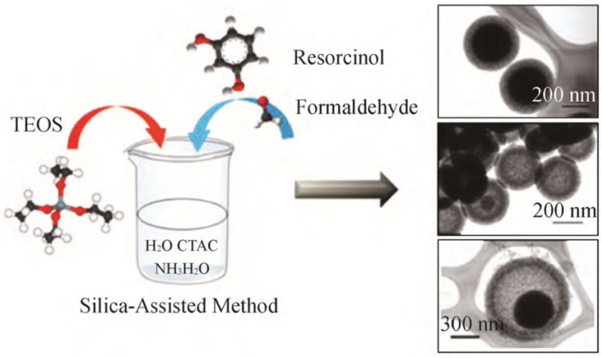

Figure 3. Synthesis of hollow carbon nanostructures via a "Silica-Assisted" strategy[27].

With a deeper understanding of the chemistry of carbon precursors, researchers began to focus on the controllable synthesis of hollow carbon spheres by simplifying the Stöber method system. In recent years, a series of universal synthetic methods for preparing hollow carbon spheres have been developed, ranging from a surfactant to no silicon oxide. Wang S *et al.*[28] reported a simple synthesis method of nitrogen-doped polybenzoxazine microsphere and nitrogen-doped carbon microspheres. The polymer microspheres were prepared by polycondensation of resorcinol, formaldehyde and 1,6-diaminohexane, and their size can be adjusted by adjusting temperature parameters. Considering that polybenzoxazine with positive charge can be adsorbed on SiO_2 surface with negative charge through electrostatic interaction. Zheng Nanfeng research group further designed a Stöber system with free surfactant to synthesize nitrogen-doped hollow carbon spheres. The synthetic route and SEM photos of the obtained products are shown in **Figure 4**. When resorcinol/formaldehyde/ethylenediamine is used as the precursor of polybenzoxazine (PB) and TEOS is used as the precursor of SiO_2, PB/SiO_2 composite shell can be directly coated on the core of SiO_2 ball in the mixed solvent of water and ethanol. In this system, ethylenediamine acts as a base catalyst to promote the hydrolysis of TEOS. The polybenzoxazine positive charge and silica oligomer with negative charge were co assembled and deposited on the surface of SiO_2 core with negative charge to form SiO_2@ PB/SiO_2 core-shell structure. The core-shell structure can be further transformed into

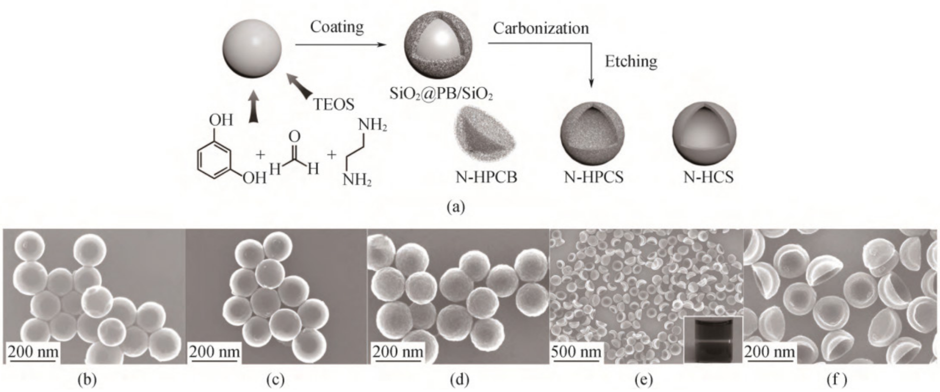

Figure 4. Sillica-assisted polybenzoxazine coating strategy for the synthesis of N doped hollow carbon spheres **(a)**; SEM images of as-obtained products **(b–f)**[29].

nitrogen-doped hollow carbon materials. The structure of hollow carbon spheres can also be changed by changing the ratio of TEOS to PB, so that they can change from spherical morphology to bowl hollow structure[29].

In addition, recently, Wan Lijun's research group prepared hollow carbon spheres by selectively dissolving 3–aminophenol/formaldehyde resin microspheres (3–AF). This method abandoned the surfactant and silica template used in the previous method (**Figure 5**)[30]. In the mixed system of water and NH_4OH, the 3–aminophenol/formaldehyde resin microspheres formed by the polymerization of 3–aminophenol and formaldehyde have uneven chemical composition. The microspheres are composed of 3–AF oligomer and high molecular weight 3–AF with high degree of polymerization, and show the core-shell structure of oligomer@ high polymer as a whole. Because the internal oligomer 3–AF can be dissolved by acetone, the prepared 3–aminophenol / formaldehyde resin microspheres can be hollow 3–AF microspheres after treatment with acetone. When hollow 3–AF microspheres are used as templates, multi shell 3–AF spheres can be further obtained by repeating the growth and dissolution process. The corresponding multi shell hollow carbon spheres can be obtained by carbonization. This work provides a controllable way for the synthesis of multi shell hollow carbon spheres. In addition, in recent years, the strategy of synthesizing polymer microspheres based on Stöber method has also been extended to other polymers, such as the successful application of polydopamine, which provides an effective way for the direct preparation of nitrogen-doped carbon based materials[31].

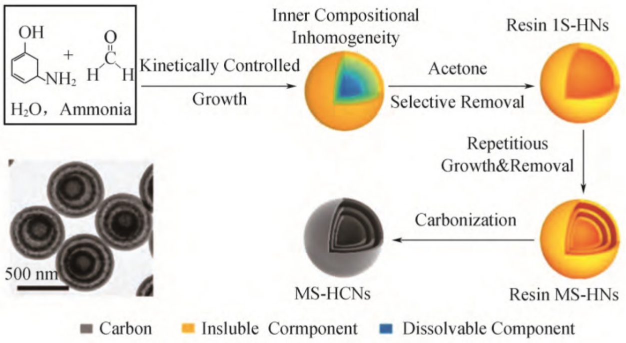

Figure 5. Fabrication of multi–shells hollow carbon spheres using 3–aminophenol/ formaldehyde resin[30].

2.2 Appearance and structure design of carbon-based hollow structure nanomaterials

Similar to the preparation of other hollow materials, hollow carbon structures with different morphologies can be obtained by controlling the morphology and structure of the template. Their morphology can be extended from simple spheres to tubular, nano sheets, polyhedron and even hierarchical structure. More importantly, the morphology and functional diversity of carbon based hollow structure nanomaterials can be enriched by reasonably designing template@ carbon precursor composites. When core / shell structural materials are used as templates, two typical sandwich intermediates can be obtained after carbon precursors coating the templates (for example: sacrificial layer@ functional layer@ carbon precursor structure and functional layer@ sacrificial layer@ carbon precursor structure). The corresponding templates can be converted into hollow core/shell carbon-based materials and Yolk@ shell hollow carbon-based structures respectively. This strategy of modifying hard template provides an effective way for the direct design of multifunctional carbon-based functional materials and greatly promotes the application of carbon-based hollow structure nanomaterials[32].

Carbon-based hollow structure nanomaterials have great application potential in the fields of catalysis, drug loading and batteries and so on. For these applications, the design of shell structure is an important aspect to further improve the application properties of hollow nanomaterials.

2.2.1 Ultra-thin shell design

In carbon-based hollow structure nanomaterials, shell structure plays a decisive role in their properties. Shell thickness directly affects the physical and chemical properties of materials, such as conductivity, specific surface area, porosity, density and available active sites. In energy storage and catalytic applications, nanomaterials with ultra-thin hollow shells are more favored by researchers. Liu R *et al.* first synthesized SiO_2@ PDA core-shell structure under alkaline conditions with dopamine as green carbon source, further carbonized and etched the core template to obtain ultra-thin hollow carbon spheres with shell thickness of only 4 nm (**Figure 6**). In addition, it prepared the Au@ C Yolk-shell structure by using Au@ SiO_2 core-shell structure as template and used in the reduction reaction of nitrophenol. The catalyst showed high catalytic activity and stability[33]. Han Y *et al.* also developed a template assisted thermal decomposition method to prepare ultra-thin hollow nitrogen-doped carbon spheres loaded with monatomic co active sites (**Figure 7**), with a shell thickness of 5 nm[34]. The ultra-thin carbon shell loaded with monatomic CO is conducive to improve the utilization of active sites. Besides, the ultra-thin shell is also conducive to the transport of reactive species. The material is used for oxygen reduction catalytic reaction under acidic conditions, showing high catalytic activity and stability.

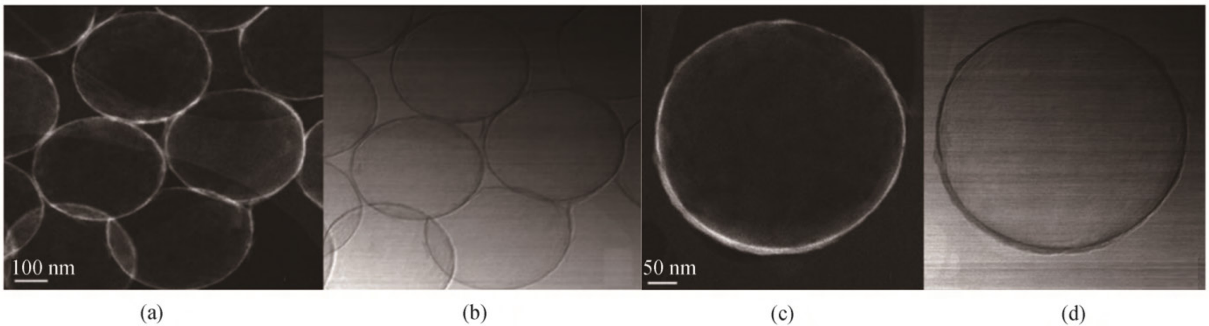

Figure 6. TEM image of super-thin hollow carbon soheres[33].

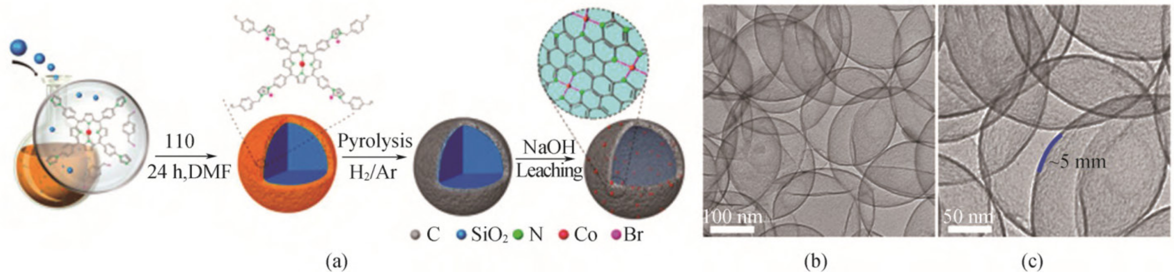

Figure 7. Schematic illustration of the fabrication **(a)** and TEM of images of super-thin hollow carbon spheres **(b, c)**[34].

2.2.2 Multi-hole shell design

Compared with the hollow micro/nano structure materials with solid shell, shell porous could improve the specific surface area of hollow structure materials. Most of the research in this field is based on the combination of soft and hard templates. When the hard template method is used to manufacture the cavity, the pore forming agent is introduced into the coating process of the shell material, and the hollow micro/nano structure material with porous shell structure can be obtained after removing the cavity template and shell pore forming agent[35]. For example, the Yu Chengzhong's research group of the University of Queensland in Australia has also successfully synthesized hollow mesoporous carbon microspheres by CO hydrolysis of organic polymers and inorganic silicon source precursors[36]. Using resorcinol, formaldehyde and silicon as raw materials, the core-shell structure material of phenolic resin/ silicon composite shell coated silicon oxide core was successfully prepared by hydrolysis/crosslinking in ethanol/water system with ammonia catalysis. Then, the template was removed by carbonization 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. Lou Xiongwen, from Nanyang University of Technology, prepared hollow mesoporous carbon by combining soft and hard templates. In alcohol/water system, multi-component composite micelles were coated on different substrates by CO assembly of carbon source dopamine, pore forming agent F127 and pore expanding agent trimethylbenzene under the catalysis of ammonia. After high temperature carbonization, mesoporous carbon shell coated core-shell nanocomposites were successfully obtained (**Figure 9**). Hollow mesoporous carbon spheres with different morphologies can be obtained after removing the substrate template[37].

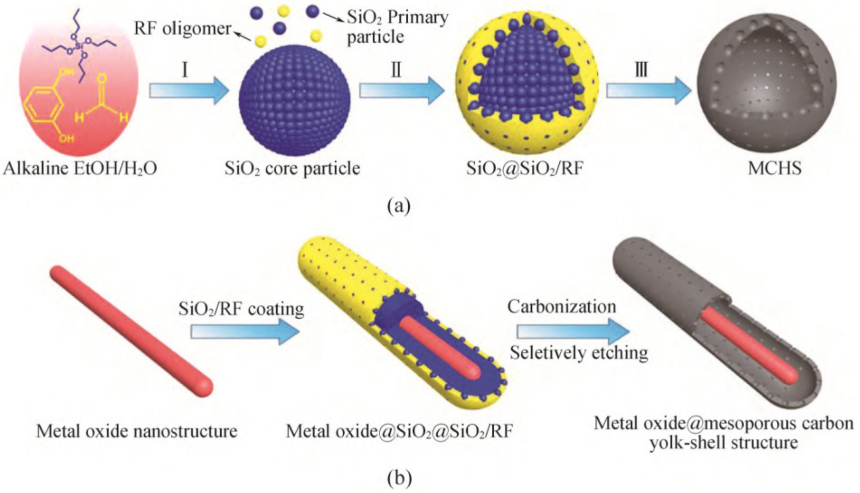

Figure 8. Fabrication of mesoporous carbon structures via a carbon/silica composite shell method[36].

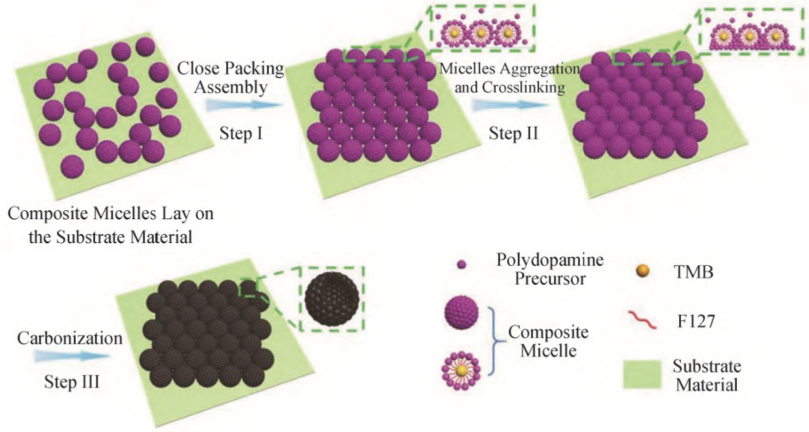

Figure 9. Fabrication of mesoporous carbon spheres via a micelle assembly atrategy[37].

2.3 Functionalization of carbon-based hollow structure nanomaterials

2.3.1 Heteroatom doping effect

In order to create more active sites and further improve the conductivity, catalytic activity and the interaction between carbon composites and reactants, the incorporation of other heteroatoms into the carbon skeleton, such as nitrogen (N), boron (B), sulfur (S), phosphorus (P) or combinations, has been widely used. Among them, due to the introduction of N element into carbon skeleton, its chemical reaction activity, conductivity, adsorption affinity for CO_2 and specific capacity for supercapacitor are much better than pure carbon materials[39,40]. The preparation methods of nitrogen-doped carbon materials can be divided into: 1) directly carbonize the precursors containing heteroatoms to obtain heteroatom doped carbon materials; 2) post treatment refers to the method of combining heteroatoms in the framework of pure carbon materials. Carbon materials are usually calcined together with precursors containing heteroatoms such as ammonia or thiourea. The biggest disadvantage of post-processing doping method is that it is difficult for heteroatoms to enter the carbon skeleton, only can modify the carbon atoms on the surface. Therefore, the first method is mostly used to synthesize homogeneous heteroatom doped carbon materials. So far, great progress has been made in the design of heteroatom doped carbon materials based on molecular level, especially the use of phenolic resin polymer precursors. A series of nitrogen-containing compounds are used to prepare nitrogen doped carbon materials, such as melamine, aminophenol, 4-amino-3-nitrophenol, 4-aminophenol, hexamethylene tetramine and 1,6-diaminohexane. In addition, some nitrogen-containing monomers, such as aniline, pyrrole and dopamine, have also been used to prepare nitrogen doped carbon materials. The content of nitrogen in nitrogen-doped carbon materials can be adjusted by adjusting the addition of nitrogen-containing precursors and calcination conditions. Similarly, when preparing 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 different elements can be introduced by combining a variety of methods.

2.3.2 Surface modification of carbon materials

Carbon materials are usually used as the carrier of catalysts to enhance the application performance of catalytic active substances, which is very important for the surface modification of carbon materials. There are two main methods to functionalize the surface of carbon: 1) deposition of nanoparticles; 2) functional group surface grafting .The loading of nanoparticles or single atoms on carbon surface is usually considered to be an effective way to adjust the interfacial properties and improve the interaction between molecules to achieve ideal catalytic and electrochemical properties. For nanoparticles highly dispersed on the surface of carbon materials, their size can be adjusted from nano scale to single atom. The smaller the size is, the more catalytic sites exposed, and the corresponding electrochemical and catalytic properties are more ideal. For example, Li Yadong's research group successfully loaded highly dispersed cobalt atoms on the surface of hollow nitrogen doped carbon spheres by a thermal decomposition method. When this material is used in oxygen reduction reaction, its atomic dispersed cobalt sites expose the number of catalytic sites to the greatest extent, and the hollow structure promotes the rapid transmission of oxygen reduction related species. The combination of this structure gives the material high catalytic performance[34]. In addition, using a similar structure, cobalt atoms were loaded on nitrogen-doped hollow mesoporous carbon spheres in the coordination mode of Co-N_5, which was used in carbon dioxide reduction reaction, showing nearly 100% carbon monoxide selectivity and high stability[41]. In order to prevent the precipitation and aggregation of precious metals on the surface of carbon support at high temperature in catalytic reaction, hollow carbon ball and carbon-based Yolk-shell structure are considered to be ideal supports. Liu R *et al.* prepared Ag/AgBr@ $SiO_{2@}$ RF core-shell structure by one-step Stöber method. After carbonizing and etching the template, Ag@ C Yolk-shell nanostructured microspheres were obtained[42]. In addition, Galeano C *et al.* limited the small-size P_t nanoparticles in mesoporous hollow carbon materials. When they were used in electrochemical oxygen reduction reaction, their stability was much better than that of commercial Pt/C[43,44].

The functional groups on the surface of carbon materials can be used as anchor points of metal catalysts and contribute to the adsorption of metals on the carbon surface. This usually allows metal species to be highly dispersed on the carbon surface and enhances chemical properties. Common methods such as oxidation, KOH activation and sulfonation have been widely used in the grafting of functional groups on the surface of carbon materials[45]. In addition, the polarity of carbon materials can also be changed by grafting functional groups. For example, the non-polar surface of carbon materials can be transformed into polar surface by introducing various polar groups such as carboxyl, nitrate, sulfonic acid and hydroxyl. For example, Wang L *et al.* etched the core-shell structure of SiO_2@ C by hydrofluoric acid and further treated with chlorosulfonic acid to obtain sulfonated hollow mesoporous carbon spheres ($ArSO_3H$-HMCS)[46].

Song D *et al.* successfully synthesized arylsulfonic acid functionalized hollow mesoporous carbon spheres by diazo coupling with furfuryl alcohol as carbon precursor by hard template method. The synthesis route is shown in **Figure 10**[47]. The grafting amount of $ArSO_3H$ on the surface of carbon materials can be controlled by the amount of sulfonic acid. The results showed that the prepared sulfonic acid functionalized hollow mesoporous carbon spheres were used as solid acid catalysts and had high catalytic activity and stability for the alcoholysis of ethyl levulinate or furfuryl alcohol. The strong Brönsted acidity of $ArSO_3H$-HMCSs plays an important role in catalytic activity. Its thin carbon shell and hollow structure shorten the diffusion distance of reactive species and promote the rapid transfer between reactants and products.

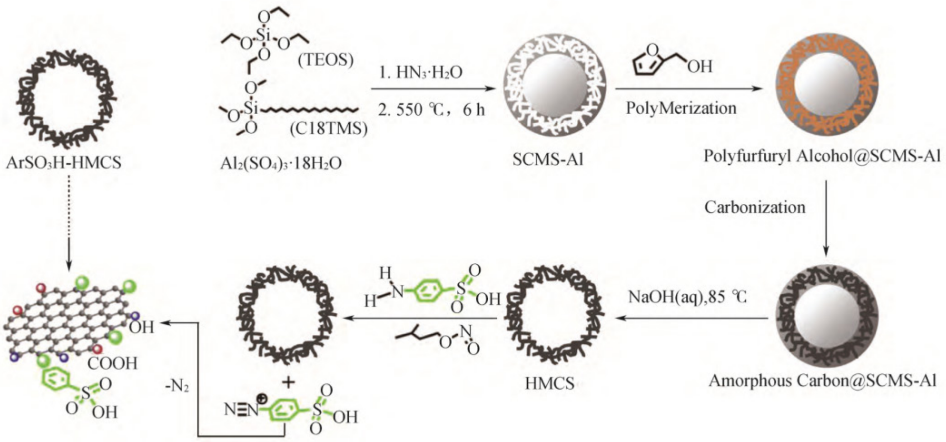

Figure 10. Fabrication of $ArSO_3$ H-mesoporous hollow carbon spheres[47].

2.4 Application of carbon-based hollow structure nanomaterials

2.4.1 Application in energy storage

For chemical batteries, high cycle stability and rate performance is a goal to be pursued in the design of any type of battery. Rapid ion and electron transport requires electrode materials to have high conductivity and open structure. Higher cycle stability requires that the electrode active material is relatively stable, and the host electrode material can alleviate the large volume expansion of the active material in the process of charge and discharge, or effectively inhibit the dissolution of some specific active materials in the electrolyte. Carbon-based hollow structure nanomaterials are widely used to load various battery electrode active materials and alleviate the volume expansion of active materials because of their unique structural properties such as high conductivity, open structure and large cavity. Hollow carbon spheres can be used as host materials to load high-capacity but unstable electrode active materials. For example, when silicon is used as the negative electrode material of the battery, the capacity decays rapidly due to the rupture of the material structure, and the cycle stability is poor[48]. Chen S *et al.* confined Si nanoparticles in hollow carbon spheres with double-layer shell structure through multi-step coating and etching strategy. The gap provided by the inner carbon shell can be used to buffer the large volume expansion change of silicon nanoparticles, while the shell helps to form a stable SEI film (**Fig-**

ure 11)[49]. Similar strategies have also been applied to protect other active materials with poor stability, such as Sn, SnO_2, MoS_2, etc.[50–52].

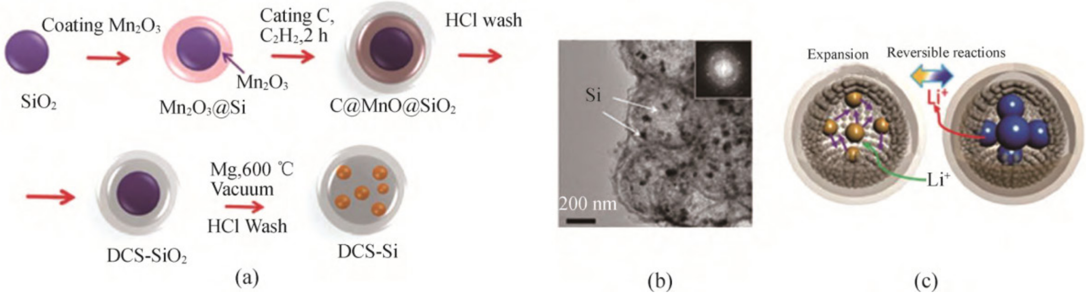

Figure 11. (a) Fabrication of silicon nanoparticles confined in double-shell carbon nanoparticles; **(b)** Corresponding TEM image of the material, with the selected area electron diffraction (SAED) pattern in the inset; **(c)** Structural change of the material during the charge-discharge process[49].

Li-S battery is considered to be one of the most potential secondary batteries because of its high energy density. Its positive active material is non-metallic S. Although it has high theoretical capacity, S has many shortcomings when it is used as battery electrode material. The low conductivity of Li-S, the shuttle effect of lithium polysulfide and high volume expansion limit the practical application of Li-S battery. In order to alleviate the above defects, hollow carbon spheres are widely used in Li-S batteries as s host materials. Carbon-based hollow structure nanomaterials loaded with polar inorganic nanoparticles are the most effective strategy to solve the defect problem of Li-S battery. Wu S *et al.* loaded cobalt oxide nanoparticles (HPCS/CoO) in hollow carbon spheres for Li-S batteries, showing excellent cycle stability. Due to the strong interaction between polar CoO nanoparticles and lithium polysulfide, the shuttle effect can be inhibited. Compared with HPCS/S electrode material, the cycle stability of HPCS/CoO/S composite electrode material is significantly enhanced. At the current density of 1.0 C, the capacity can still reach 629 $mAh{\cdot}g^{-1}$ after 1,000 cycles. On the contrary, after 1,000 cycles, the specific capacity of HPCS/S electrode 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 composite materials for Li-S battery, which effectively solved the defect of S cathode and achieved excellent battery performance[60–63].

Unlike storing lithium ions in the negative electrode material of the battery, lithium metal batteries directly use metal lithium as the negative electrode material. Compared with the traditional graphite anode material for lithium ion batteries, lithium metal has a higher specific capacity (3,860 $mAh{\cdot}g^{-1}$)[64]. When the lithium metal negative is coupled to other high capacity positive materials (such as oxygen and sulfur cathode) are coupled,

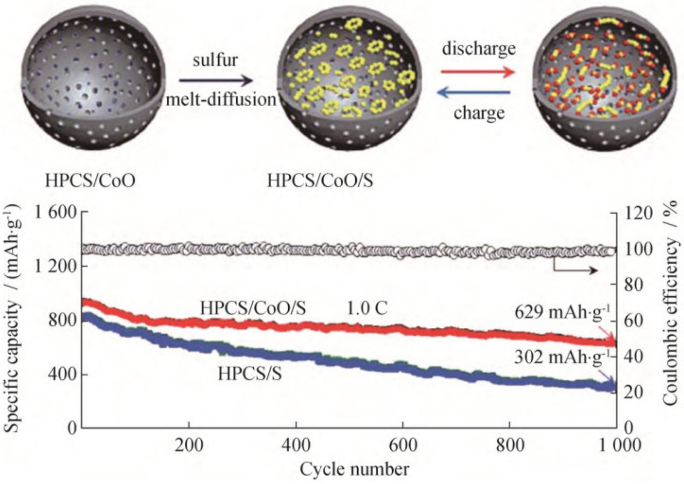

Figure 12. Schematic illustration of the fabrication of HPCS/CoO/S and cycling performance of HPCS/CoO/S for Li-S battery[59].

strong attractive energy density can be obtained (such as 3,500 Wh·kg^{-1} for Li-O_2 battery and 2,600 Wh·kg^{-1}S battery for Li-S battery)[65]. Although lithium metal has these advantages, its inherent defects are also obvious, including high reaction activity, huge volume change during circulation and the formation of lithium dendrite[66]. In order to solve this problem, the surface protection of lithium metal is essential, and hollow carbon microspheres are ideal host materials to solve this problem. Because it is difficult to control the morphology and deposition position of lithium metal during deposition, the consistent deposition of Li metal in hollow carbon spheres is a great challenge. Until recently, researchers first deposited Au nanoparticles in hollow carbon spheres, and then successfully controlled the deposition of metal lithium in hollow carbon spheres with Au as seed (**Figure 13**). Since the direct contact between lithium metal and electrolyte is avoided, this limited space can effectively improve the stability of electrochemical cycle of lithium metal and minimize the adverse side reactions between lithium metal and electrolyte. The cycle performance of lithium metal battery is improved, the coulomb efficiency in carbonate electrolyte is up to 98%, and it has excellent cycle stability in more than 300 cycles[67].

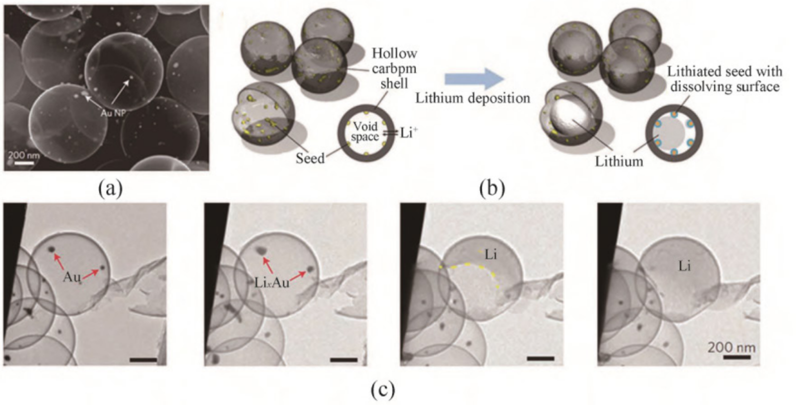

Figure 13. (a) TEM images of gold nanoparticles trapped inside hollow carbon nanospheres; **(b)** Lithium deposition process inside the hollow carbon structure; **(c)** Corresponding TEM images of the lithium disposition at different stages[67].

2.4.2 Application in electrocatalysis

Electrocatalysis is an important process in the field of clean energy conversion (fuel cell, water decomposition and metal air cell). However, due to the slow kinetic processes such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), these fields are greatly limited in practical application. In addition, carbon dioxide reduction, methanol oxidation and nitrogen reduction are also key factors in the process of renewable energy conversion. Carbon-based hollow structure nanomaterials with high conductivity can improve the charge transfer efficiency. Besides, hollow structure and porous structure can improve mass transfer efficiency. Based on the unique structural characteristics of carbon-based hollow structure nanomaterials, researchers generally believe that carbon based hollow structure nanomaterials are one of the best candidates for electrocatalysts with high activity and stability.

Oxygen reduction reaction (ORR) plays a very important role in metal air cells and fuel cells. Pt electrocatalysts show excellent ORR activity under acidic and alkaline conditions, but due to its high cost and poor stability, the mass production and further practical application of precious metal Pt are greatly limited. In recent years, researchers are committed to the synthesis of electrocatalysts with low cost and stable performance. Carbon-based hollow structure nanomaterials have attracted more and more attention because of their low price, high activity and stability. Nonmetallic carbon-based materials can modify their electronic structure and chemical activity by doping various heteroatoms such as N, S and P. The electronegativity and atomic radius difference between heteroatoms and carbon atoms change the electronic structure of C atoms adjacent to heteroatoms, which is conducive to the adsorption and electron transfer of oxygen species and enhance their ORR activity. For example, Lou Xiuwen's research group developed the strategy of self-assembly of polymer block copolymer F127 and polydopamine composite micelles to synthesize ultra-thin hollow nitrogen doped carbon spheres. The ultra-thin shell with single-layer mesoporous structure ensures the rapid progress of mass transfer process and high catalytic activity[37]. Although heteroatom-doped carbon materials exhibit stable and efficient ORR properties in alkaline solution, their ORR activity under acidic conditions is not satisfactory[68]. In order to solve this problem, carbon-based materials modified by non-noble metals (Fe, Co and Ni) have been widely studied.

2.4.3 Carbon-based hollow structure nano materials being used as nano reactors for catalytic reactions

It is very important to design a suitable reactor in chemical reaction engineering. In order to obtain the best reaction conditions, hydrodynamics, mass transfer, heat transfer and reaction kinetics must be considered. The development of nanotechnology makes the reaction vessel change from macro to micro structure, which opens the concept of new nano reactor. From the perspective of chemical engineering, the catalysts designed and prepared are regarded as nano reactors. Compared with conventional reactors, nano reactors have the advantages of parallel chemical reactions, avoiding the formation of adverse products and enhancing catalytic performance. A plurality of reaction sites can be controllably located in different spatial positions of the nano reactor. For example, in a hollow carbon-based catalyst, a plurality of catalytic sites can be located on the inner and outer surfaces of the carbon shell, the voids and anisotropic positions of the carbon particles, so as to obtain the best catalytic performance. Compared with solid carbon-sphere catalyst, hollow carbon-sphere catalyst nano reactor has the following advantages: 1) catalytically active species can be loaded in the cavity to prevent the migration and agglomeration of active particles during the catalytic reaction, resulting in the reduction of catalytic activity; 2) the selective catalytic activity can be further enhanced by the regulation of shell structure; 3) compared with the same mass of bulk catalyst, the mass transfer process in the catalytic reaction process can be further improved; 4) by adjusting the hydrophilicity/hydrophobicity in the cavity, the reaction products are enriched in the cavity, so as to improve the catalytic reaction rate[69].

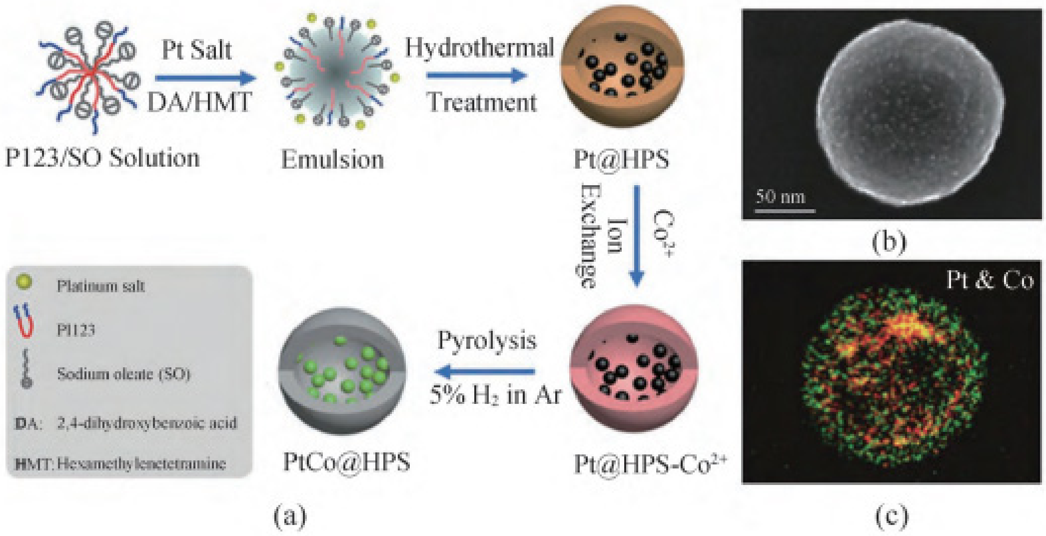

Figure 14. (a) Schematic illustration of the synthesis of PtCo@ C Yolk-shell micro-spheres; **(b)** TEM image; **(c)** EDX mapping images of PtCo@ C Yolk-shell micro-spheres[70].

Selective hydrogenation is very important in organic synthesis, such as the synthesis of epoxy compounds. Most of the catalysis must be carried out at high temperature, which makes the active nanoparticles easy to be sintered and lose activity in the reaction. Schüth and his collaborators developed a simple method to confine 4 nm PtCo nanoparticles in the hollow carbon sphere cavity (**Figure 14**)[2]. Using this material as catalyst, the conversion efficiency of 5-hydroxymethylfurfural to 2, 5-dimethylfuran is as high as 100% in 10 minutes. After 2 h, the yield of 2,5-dimethylfuran was as high as 98%. In another work, Wang GH *et al.* successfully prepared Pd@ C Yolk-Shell structure catalysts by hydrothermal treatment of emulsion containing polymer precursors. The emulsion contains P123/sodium oleate/$PdCl_4$2-, 2, 4 dihydroxybenzoic acid, and the emulsion of the polymer precursor of hexammethyltetramine[70] Recently, Tian H *et al.* also reported a Yolk-Shell structure submicron reactor loaded with metal nanoparticles, and its structure is Pd@ Zn/C Yolk-Shell structure[71]. When used as a catalyst for hydrogenation of phenylacetylene to styrene, the selectivity of the catalyst can reach 99%, and has high conversion and excellent catalytic stability.

3. Summary and prospect

In the past ten years, carbon-based hollow structure nanomaterials have been developed by leaps and bounds, and have achieved fruitful results in synthesis, characterization and application. In this paper, the basic synthesis strategy, structural design, material functionalization and main applications of carbon-based hollow structure nanomaterials are summarized. The unique structure of carbon-based hollow structure nanomaterials shows great potential application value in many application fields. Because of this broad application prospect, the research, development and application of this kind of materials is still a hot spot in the research 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 load components of carbon-based hollow structural materials. According to different application requirements, carbon-based hollow structural materials with desired physical properties were prepared. Understanding the structure-activity relationship between material structure and application properties is not only the driving force to promote the development of carbon based hollow structure nanomaterials, but also a major challenge in this field.

Conflict of interest

The authors declare that they have no conflict of interest.

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