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Current Trends in Designing and Applications of Nanoporous Carbon Spheres: A Mini Review

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Mini Review

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Abstract

Great progress has been made in the synthesis and applications of nanoporous carbon spheres in the recent years. In this brief review, we will review the synthesis and applications of nanoporous carbon spheres, and further describe their advantages and disadvantages. The synthesis techniques are mainly introduced in the review including the Stöber method and those based on templating, self-assembly, emulsion and hydrothermal carbonization, while applications are described shortly. We cover the key applications of these nanoporous carbon spheres, including adsorption, catalysis, separation, energy storage and biomedicine. In the end, we put up some outlook in the improvement of the synthesis methods and commercial applications of nanoporous carbon spheres.

Keywords: Nanoporous Carbon Spheres; Stöber Method; Self-Assembly; Adsorption; Catalysis

Introduction

Porous carbon materials have attracted considerable attention because of their applications in a wide range of areas, including energy storage and conversion, adsorption, catalysis, sensor technology, and controlled drug release and cellular delivery. As an important class of novel porous carbons, nanoporous carbon spheres (NCS) have become a research hotspot due to their unique nanospherical morphology, large surface area and pore volume, good electrical conductivity, and high physical and chemical stability. In recent years, with the rapid growth in the synthesis and applications of NCS [1-7], these materials present great utilitarian value for catalysis, adsorption, water and air purification, and energy storage and conversion. Currently, there are several strategies for preparing NCS and multi-component CS, such as templating [4-6], hydrothermal carbonization (HTC) [7], emulsion polymerization [8], self-assembly [9] and the Stöber method [10-13]. As a result, NCS have been fabricated with particle sizes ranging from nanometres to micrometres, diverse morphologies, pore sizes ranging from micropores (below 2 nm) to mesopores (2-50 nm) and macropores (>50 nm), and controlled pore orientation. Moreover, functionalized NCS have been synthesized by surface modification, heteroatom doping and graphitization [4-13].

The NCS can be classified by their morphological as solid NCS (s-NCS), hollow NCS (h-NCS), core-shell NCS (cs-NCS) and york-shell NCS (ys-NCS). This Review briefly summarizes the key developments in synthesis and applications of NCS, and discusses the impact of their functionalization on the growing range of applications, including adsorption, catalysis, energy storage and nanomedicine. In the end, we shortly elaborate the applications and future of the development of NCS.

Synthesis of Nanoporous Carbon Spheres

There is a wide variety of methods for preparing NCS, including hard and soft templating, HTC, emulsion polymerization, self-assembly and Stöber synthesis (Table 1). Although a number of other methods such as direct pyrolysis of hydrocarbons or chemical vapor deposition (CVD) have been used to synthesize NCS, these result in polydisperse NCS and are thus more demanding from an experimental viewpoint. Further integration of the above-mentioned methods would be desirable to discover new ways of synthesizing NCS with higher levels of complexity and functionality.

Hard and Soft-Templating

As shown in Figure 1(i), the hard-templating (HT) strategy mainly contains the following steps. First, prepare mesoporous silica spheres. Second, fill their pores with suitable carbon precursors. Finally, silica dissolution with NaOH or HF solutions. Kim et al. were the first to publish the paper about the HT synthesis of ordered mess-CS which is using 3D cubic-ordered mesoporous silica named MCM-48 as a hard template [4]. Nowadays, we expect to discover more appropriate precursors and hard templates. As shown in Figure 2, preparing hollow NCS also involves three main steps. Synthesizing hard templates, coating the templates with specific carbon precursors and removing the templates. Current understanding in this area allows that HT is the most straightforward way of synthesizing h-NCS [13]. However, there is a major drawback of HT method that it is difficult to complete the procession of forming special hard templates and use hazardous chemicals such as HF and NaOH, which limits its popularity.

Compared with the HT method, soft templating (ST) does not need preparing and removing templates [5,6,14-17]. Up till now, the reports on the ST technique of preparing mesoporous CS (meso-CS, Figure 1(ii)) are rare so this method is inappropriate for scaling up. What is similar to the HT synthesis is that the ST concept has been also used to synthesize h-NCS (Figure 1(iii)) [18]. However, its low yield and relatively high cost make it a great challenge.

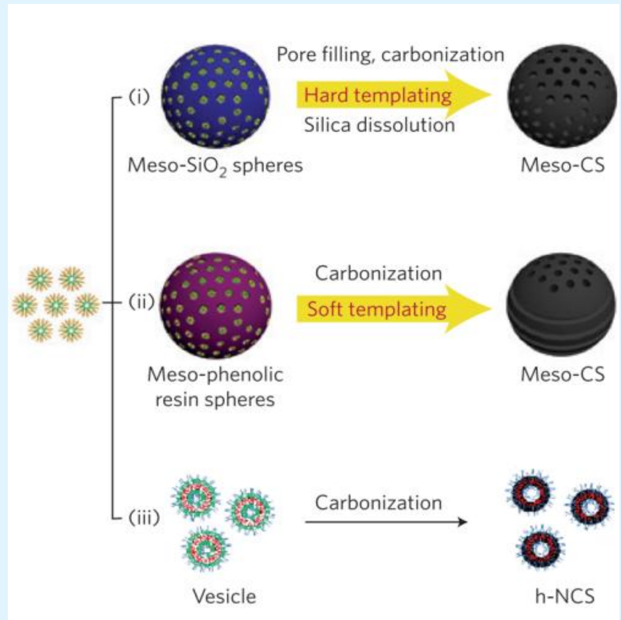

Figure 1: Hard and soft templating method for fabrication of CS [18]. Pore filling, carbonization, silica dissolution are labeled as the step a, b, and c in the HT strategy.

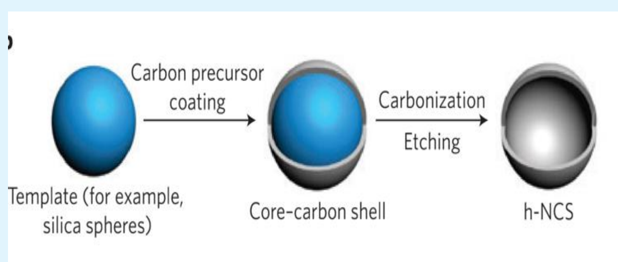

Figure 2: Preparation of h-NCS using a soft-templating method.

Synthesis Method	Types of NCS	Carbon Precursors
HT	h-NCS [13] ys-NCS	Glucose, sucrose, dopamine, 1-alkyl-3-methylimidazolium bromide, phenolic resins (phenol-formaldehyde, resorcinol-formaldehyde)
ST	h-NCS [6,17,18] cs-NCS ys-NCS	Phenolic resins (phenol-formaldehyde, resorcinol-formaldehyde), cyclodextrins
HCT	h-NCS cs-NCS [11]	Biomass derivatives (glucose, cyclodextrins, fructose, sucrose, xylose), furfural alcohol, phenolic resins (phenol-formaldehyde, melamine-formaldehyde, resorcinol-formaldehyde-hexamethylenetetramine), pyrrole
Microemulsion polymerization	micro-CS [8,22,23]	Styrene,1,2-divinylbenzene
Stöber method	h-NCS [13] cs-NCS [11] ys-NCS [19]	Phenolic resins (resorcinol-formaldehyde, aminophenol-formaldehyde, phloroglucinol-terephthalaldehyde, resorcinol-melamine-formaldehyde), dopamine
Direct pyrolysis	micro-CS [21]	Benzene derivatives (benzene, nitrobenzene, aniline, naphthalene, anthracene, phenanthrene, pyrene), polyacrylonitrile
Microwave treatment	micro-CS	Phenolic resins (resorcinol-formaldehyde, resorcinol-melamine-formaldehyde)

Table 1: Carbon precursors and methods.

HTC Synthesis of Micro-CS and H-NCS

Currently, there are great interests in exploring how to prepare CS by the HTC of biomass derivatives at lower temperatures (160-200°C, Figure 3) because of its simplicity, sustainable and versatile chemistry, low cost and high efficiency [7]. In contrast with templating, the steps of HTC are more complex involving dehydration, condensation, polymerization and aromatization. Using this method, we can obtain micro-CS with tunable particle size scoping from 200nm to 5000nm and a series of various functionalities hinging on carbon precursors used (Table 1) [7,19,20]. As a viable way of preparing CS, HTC also have problems in any way. For example, its application is still limited in controlling porosity and CS size lacking of the proper biomass-derived carbon precursors.

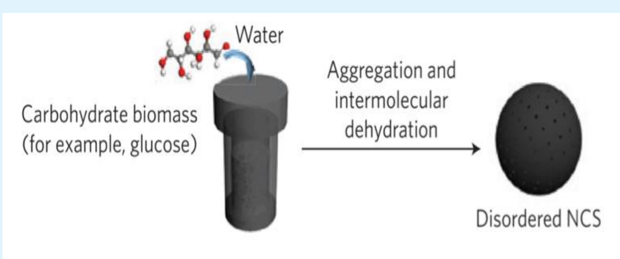

Figure 3: HTC synthesis method for fabricating the CS.

Microemulsion Polymerization Synthesis

Microemulsion polymerization synthesis is a most popular method for producing mono disperse polymer spheres, this strategy is a big challenge to researchers who have failed to turn colloidal spheres into their carbonaceous analogues owing to thermolysis and serious particle agglomeration [21,22]. Adding divinylbenzene crosslinking could overcome these issues (Figure 4).

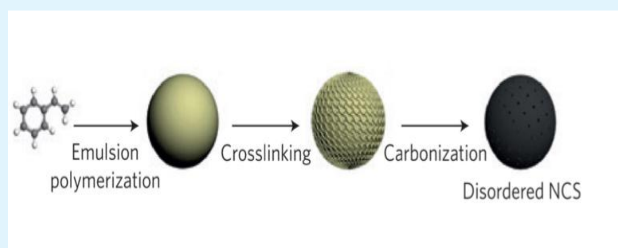

Figure 4:Microemulsion polymerization synthesis of CS [8].

Extension of the Stöber Method

Extension of the Stöber method is a great breakthrough in the development of NCS which was completed in 2011. Recently, researchers discovered that the sol-gel formation of silica spheres is similar to the process of forming phenolic resin polymer [10]. Why we can believe this conclusion is because of the successful preparation of monodisperse phenolic resin spheres with tunable particle sizes through the Stöber process [10]. Making these polymeric spheres carbonized supports micro-CS high yield and its tunable particle size can range from 150-900nm (Figure 5(i)). Surprisingly, it is by this technique that we obtain the NCS with various functionalities [11-13]. Some compounds such as 3-methylphenol, 1,3,5-trihydroxybenzene and 3-aminophenol which are the derivatives of phenol were used to product phenolic resin spheres highly monodispersed and in the meantime develop the corresponding NCS whose molecular particle size is controlled [23,24]. We usually use melamine, resorcinol and formaldehyde as precursors, creating a range of melamine-phenolic resin-based spheres and N-doped NCS which is special having particular particle sizes, microporosity and nitrogen content in the framework [25].

In addition, the Stöber method also provides opportunities for the design of h-NCS. There is an example in the Figure 5(ii). Adding colloidal silica helps create the same spherical mesopores in CS. However, this method is limited by selecting available carbon precursors. Besides, in the procession of the Stöber, ammonia is one of the basic catalysts, which makes it difficult to extend the popularity of this method.

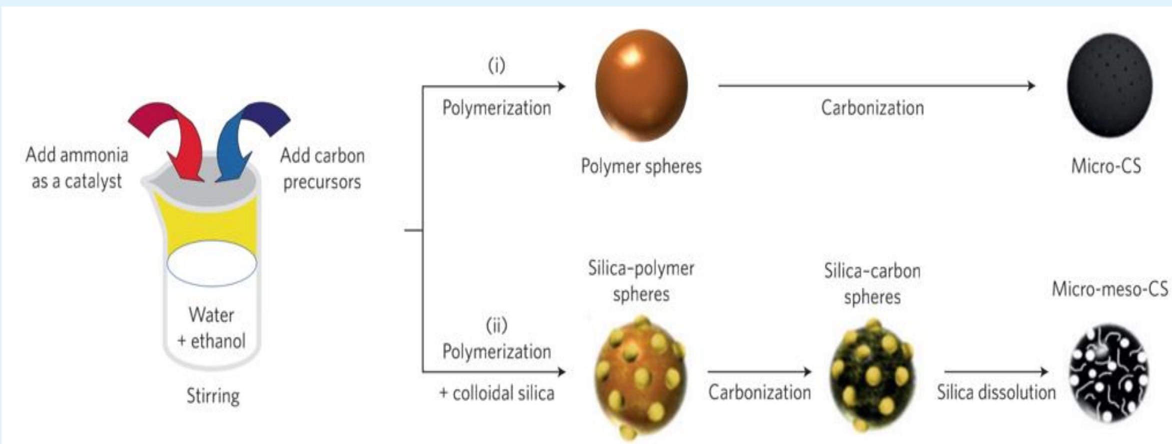

Figure 5: NCS prepared by using the Stöber method [11].

The Selection of Precursor in the Design Process of NCS

Selecting appropriate precursor is of great importance for the design of NCS, especially for those with particular composition, framework and functionality. There are a variety of precursors shown in Table 1, which are able to be used for the synthesis of NCS with the methods of templating, HTC and Stöber. For instance, the preparation of N-doped NCS needs a kind of biocompatible precursor such as dopamine. In addition, phenolic resins integrate several advantages including high thermal stability and easy conversion to carbon materials. Therefore, these resins through special process can be as the excellent precursors for the design of NCS. What' more, it was used for fabricating the NCS at the molecular level that can be synthesized by selecting proper phenol and aldehyde derivatives (Table 1).

Applications

Carbon-based materials are the most attractive material types in both fundamental research and industrial applications, partly because of their well-controlled nano-morphologies. In the past two decades, researchers have witnessed a number of breakthroughs in carbon research: fullerenes, carbon nanotubes, and graphene. Nowadays, carbon nanospheres are attracting more and more attention worldwide due to their excellent performance in various fields: drug delivery, heterogeneous catalysis, encapsulation of support and electrode materials, energy conversion and storage, nanomedical, and environmental science. Actually, spherical carbon is an old material, whereas controlling carbon spheres in the nanometer range is a recent story. Here, we present a brief summary of the various applications for NCS (Figure 6). Throughout this article, a special emphasis is placed on the possible modulation of spherical structures at the nanoscale, and we wish to inspire many more designs and applications of carbon nanostructures in the near future. Due to the unique morphological and structural properties of NCS, there are many current applications which we will give a brief summary.

Energy Storage and Conversion

In brief, we can take electrodes and electrocatalysts for examples. Carbon nanomaterials can be as electrodes in super capacitors, lithium-ion batteries and Li-S batteries, and as electrocatalysts for hydrogen evolution reactions and oxygen reduction reactions [27]. In the Table 2, we list the key properties of NCS for specific applications.

Applications	Preferred properties	Type of NCS
Super capacitors	Hierarchical porous structure , large surface area, high electronic conductivity, heteroatom doping	cs-NCS
Lithium-ion batteries	Facilitated Li^+ transport, large surface area, short diffusion distance, heteroatom doping, suppressed agglomeration of active particles, buffer space for volume expansion	h-NCS ys-NCS
Li-S batteries	Facilitated Li^+ transport, large surface area, short diffusion distance, avoid sulphuric melting	h-NCS ys-NCS meso-NCS
Fuel cells	Fast gas diffusion, high porosity, large surface contact angle, high air permeability, rapid water vapor diffusion, high electronic conductivity, enhanced oxidative stability	cs-NCS ys-NCS
Catalysis	Fast diffusion of reactant and products, highly exposed catalytic active sites, homogenous environment, recyclability	cs-NCS ys-NCS
CO_2 capture	Large surface area, narrow pore size distribution, basicity of the framework, fast diffusion	Super microporous basic ys-NCS
Biomedical	Appropriate particle size, multifunctional ability (fluorescence, drug, antibody, diagnosis), low toxicity	Multifunctional carbon nanospheres

Table 2: Preferred properties and types of NCS for specific applications.

Biomedical Applications

Compared with other types of carbon such nanotubes and graphene, NCS will cause no or minimal damage to cells because of their low cytotoxicity and no-sharp edges. For example, NCS can be used to deliver drugs, contrast agents and target molecules such as genes. In addition, owing to NCS's hydrophobic properties, they exhibit better affinity towards hydrophobic drug molecules.

Catalytic and Adsorption-Based Applications

Functionalized NCS can be used as heterogeneous catalysts or catalytic supports for a variety of reactions like Friedel-Craft alkylation [28], hydrogenation, Fischer-Tropsch synthesis and photocatalytic reactions. The porous carbon shell of h-NCS or ys-NCS acts as a physical barrier but still allows reactants and products to travel between the catalyst surface and the bulk phase containing the reactants. Moreover, carbonaceous materials have high chemical stability in various reaction environments (such as acidic and basic). Compared with other supports such as SiO_2, Al_2O_3 and TiO_2, interactions of NCS with active metal catalysts are weaker, which prevents the formation of mixed compounds between metal catalysts and supports [27].

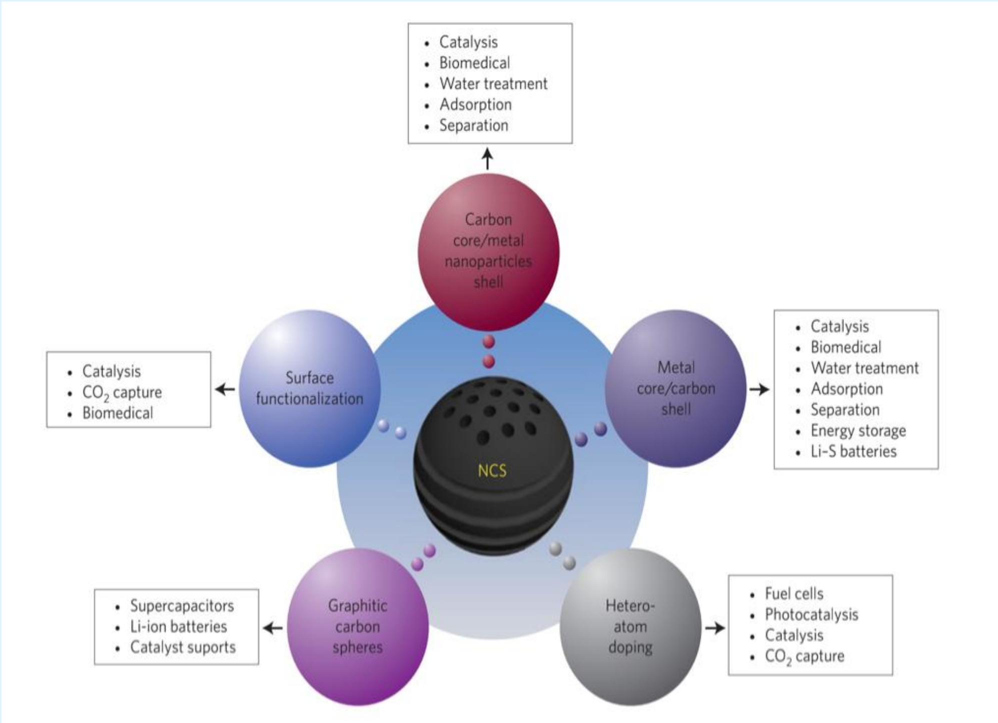

Figure 6: Various applications of NCS [26].

Outlook and Summary

From the researches in recent years, there is a great development in the synthesis and application of NCS, especially towards controlling the sizes of particle and pore. Templating, HTC, Stöber method which are all the available techniques for preparing NCS, but they also have some limits. Thus, in spite of a mass of achievements in NCS, we need badly new synthesis methods and applications. Some techniques described above are difficult to scope up, while for the future applications the design of NCS at the molecular lever is an important basis. In the near future, there is great interest in developing carbon nanostructures beyond carbon nanospheres for many more applications.

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