QILU UNIVERSITY OF TECHNOLOGY

本科毕业论文

Synthesis of mesoporous silica hollow spheres with complex morphology

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Content

Abstract

Nowadays, mesoporous materials with hierarchical structure and definite morphology have attracted great attention[1-7]. Mesoporous materials research not only can be applied to practical applications, but also reveal the basic mechanism of biomineralization. Among the different types of mesoporous materials, hollow spheres are widely used in catalysis, drug delivery, and controlled-release applications.

In this paper, we use Polystyrene spheres as hard-templating agent, with the addition of the anionic surfactant N-lauroylsarcosine sodium (Sar-Na) to create mesopores with complex morphology on the surface of silica hollow spheres. For the growth of mesoporous silica hollow spheres with budding morphology, Wang[8] has been synthesized using the emulsion template method. This article uses a new synthesis method, namely use the PS microspheres as a template agent, and the occurrence of carboxylic acid and amino groups follows acid-base reaction. Calcination at high temperature to form a hollow structure of mesoporous silica hollow spheres. And using Sar-Na as a templating agent in combination with a part of hydrochloric acid to form an amphoteric polar oil[9], the Sar-H in the form of droplets, which is often used in cosmetics and pharmaceutical industry due to Sar-Na biodegradability and low toxicity. According to the pioneering study of anionic surfactant-templated mesoporous silica (ASM) by Tatsumi and colleagues, the co-assembly of anionic surfactant (S) and silica precursor (I) follows $S^-N^+ \sim I^-$. The pathway, in which N is a co-structural directing agent, such as APMS[10-13]. Sar-H oil swells the hybrid gum and converts the columnar micelle phase into a lamellar phase, thereby producing buds of bubble-like intermediate structures. The added of the silica precursors (3-aminopropyltriethoxysilane (APES) and tetraethyl orthosilicate (TEOS)) surrounds PS pellets to form hollow spheres. This paper also studied the effect of different hydrochloric acid content conditions on the morphology and structure of mesoporous silica. And confirmed the practical application of mesoporous silica hollow spheres.

Key words: Mesoporous silica; Dynamic assembly; PS; Complex morphology

摘　要

近来，具有层次结构和明确形态的介孔材料引起了人们的广泛关注[1]介孔材料的研究不仅可以运用于实际应用中，也可能揭示生物矿化的基本机制。在众多类型的介孔材料中，空心球因其在封装，给药和控释应用中的潜在用途而具有重要意义。

在本论文中，我们使用 PS 小球为硬模板剂，连同加入一种阴离子表面活性剂十二烷基氨酸钠(Sar-Na)来制造表面有复杂形态的介孔二氧化硅空心球。对于出芽形貌的介孔二氧化硅空心小球生长已有 Wang[2] 使用乳液模板法合成，本文使用一种新的合成方法，即使用 PS 微球为模板剂，发生了羧酸与氨基的酸碱反应，高温煅烧后形成介孔二氧化硅空心球的中空结构。并使用 Sar-Na 为模板剂结合一部分盐酸形成一种两性极性油[3]，表现为液滴状态的 Sar-H，由于 Sar-Na 生物降解性和低毒性，其常用于化妆品和制药工业。根据 Tatsumi 及其同事对阴离子表面活性剂模板化介孔二氧化硅（ASM）的开创性研究，阴离子表面活性剂（S）和二氧化硅前体（I）的共同组装遵循 $S^-N^+ \cdots I^-$ 途径，其中 N 为一种共结构导向剂，如 APMS[4]。Sar-H 油使杂合胶溶胀并将柱状胶束相转变成层状相，从而产生泡状中间结构的芽。加入的二氧化硅前体（3-氨基丙基三乙氧基硅烷（APES）和原硅酸四乙酯（TEOS））包裹 PS 小球以形成中空球体。本文还对不同盐酸含量条件下的合成，对介孔二氧化硅的形貌，结构的影响进行研究。

关键词：介孔二氧化硅　动态组装　PS　复杂形貌

Chapter 1　Introduction

1.1 Mesoporous silica material

The definition developed by the International Union of Pure and Applied Chemistry (IUPAC)[14]: Porous materials with pore sizes between 2 and 50 nm are called mesoporous materials. Compared with other porous materials, mesoporous materials have the following four basic characteristics: 1. highly ordered pore structure; 2. narrow pore size distribution, and continuously adjustable pore diameter in a relatively wide range (2~50nm); 3. high porosity and high specific surface area; 4. can have different structures, properties and pore wall components. Therefore, these characteristics make it an important application in the fields of chemical industry, information technology, biotechnology, and environmental energy, and it also provide models for the study of basic problems such as physical and chemical behaviors of substances. From the appearance of mesoporous materials to the present, it has been widely used in the loading of catalytically active components, and it is widely used in the field of heterogeneous catalysis.

Through the classification of chemical composition elements, mesoporous materials can be divided into two major categories containing silicon-based and non-silicon-based components, the latter including sulfides, transition metal oxides, phosphates, and carbon. Compared with silicon-based mesoporous materials, non-silicon-based mesoporous materials have poor thermal stability during the preparation process. When the template is calcined, the pore structure is easily collapsed, and its pore volume and specific surface area are also small. Both are relatively small, the synthesis mechanism has not been completely clarified, and the practical application value is not significant. Therefore, the main research focus at present is focused on the mesoporous silica material having a silicon-based composition.

Mesoporous silica has important significance not only in the preparation and application of functional materials, but also in biomineralization and biomimetic material chemistry research. Therefore, it has been a hot topic in the synthesis of mesoporous materials. The mesoporous silica material is first self-assembled with a polymer (containing a hydrophilic and a hydrophobic group) and a polymerizable inorganic precursor under certain synthesis conditions to form an organic/inorganic composite having a mesostructure, and then used for baking or solvent extraction and other methods remove the organic templating agent and the remaining space constitutes the mesopores.

Mesoporous silica can be divided into the following two types[15] from the perspective of microstructure: One type is an unordered mesoporous solid, which represents a variety of silica xerogels and aerogels, such mesoporous channels shape is irregular, but the interior of the channel is interconnected and the shape is complex. There is no regularity. The hole shape can be similarly described by the shape of the single-mouth round bottom flask. The place of the fine bottle mouth is similar to the junction between the holes. The existence of disordered mesoporous silica in the macroscopically manifested as powders, films, blocks and even platelets, these macroscopic morphology states are of crucial importance for the specific application of mesoporous materials. The other is the ordered mesoporous silica represented by MCM-41 reported by Kresge CT et al [15]. Its structural characteristics are: the pore diameter is uniform and arranged in order according to the hexagonal phase. Under various preparation conditions, the pore size can be maintained in the range of 1.5 to 10 nm and can be continuously adjusted. The pores of ordered mesoporous silica can be roughly classified into the following three categories: 1. Interlayered holes arranged in parallel; 2. Cylindrical holes arranged in a direction (holes are straight channels); 3. Three-dimensional arrangement of polyhedral holes (three-dimensional channels running through each other).

The template method is the most effective method for preparing mesoporous silica hollow spheres, including soft template method and hard template method. The former is the synthesis of hollow sphere materials using surfactants, vesicles or microemulsions formed in solution in micelles or other aggregated states as templates. This method requires high control of the synthesis process. Subtle changes in the synthesis conditions can lead to uneven product morphology and structure. In contrast, the preparation process based on the hard template method is easily controlled by coating a layer of mesoporous silica on the surface of organic polymer, metal or non-metal oxide beads, and then removing the inner core material to obtain silica. In the hollow sphere material, the product obtained by this method is not only structurally uniform, but also the structural parameters can be adjusted to some extent. Typical tasks include: Qi et al. used polystyrene (PS) pellets as hard templates to synthesize mesoporous silica hollow spheres of different sizes.

1.2 Polystyrene Microsphere

Surface-functionalized polymer microspheres are easily combined with enzymes, proteins, nucleic acids, etc. due to the presence of active groups such as carboxyl, amino, or hydroxyl groups on the surface, making them widely used in biology, chemistry, materials, medicine, and the like. Monodisperse polystyrene particles have a wide range of applications in scientific research due to their high monodispersity, ideal spherical shape, and easily controlled particle size and surface electrical properties.[16, 17]

In this article, soap-free emulsion polymerization method[18] is used to synthesize polystyrene microspheres. Soap-free emulsion polymerization is a new polymerization technique that is improved in traditional emulsion polymerization methods. It means that no emulsification is performed during the reaction process. Emulsion polymerization with agents or with only a small amount of emulsifier at a concentration below the critical micelle concentration of the emulsifier[19]. The

addition of hydrophilic monomers can replace emulsifiers and allow rapid polymerization[20].

Using styrene and acrylic acid as monomers, potassium persulfate as initiator and deionized water as dispersion medium, carboxylated polystyrene microspheres were prepared by soap-free emulsion method. Transmission electron microscopy and dynamic light scattering results showed that the obtained microspheres were obtained. The diameter is uniform; changing the comonomer acrylic ratio, initiator dosage, polymerization temperature and stirring speed can get carboxylated polystyrene microspheres with a particle size of 150 to 400 nm. The surface carboxyl group content of the microspheres can reach 0.315 mmol/g. It meets the practical requirements for the construction of sensitive components such as microsphere array chips.

Nucleation mechanism[21]: At the beginning of the reaction, the hydrophilic monomer is copolymerized with a hydrophobic monomer dissolved in the aqueous phase to form an amphoteric oligomer radical. After reaching the critical chain length, it precipitates from the aqueous phase and forms a nucleus. The monomer diffuses into the core, polymerizes into micelles, and absorbs monomers from the aqueous phase, which then initiates growth in the micelles. The water in the soap-free emulsion polymerization is a continuous phase, and the bulk and initiator particle groups are hydrophilic, and are preferentially distributed on the surface of the microspheres. Therefore, no emulsifier is added in the reaction, and the microspheres can also exist in a stable manner without soap. Emulsion polymerization has many advantages, such as the preparation of microspheres with surface-enriched hydrophilic groups and core-shell hydrophobic-hydrophilic microspheres, with clean surfaces and good monodispersity [22-24]. At the same time as the radial testing and drug carriers, it solves the traditional difficulties of post-emulsion polymerization and the adverse effects of emulsifiers on product performance; it reduces production costs and reduces environmental pollution[25]. However, there are also some disadvantages. Because no

emulsifier or a small amount of emulsifier is added in the soap-free polymerization reaction system, the solid content of the product is generally low, and there are still difficulties in the application of coatings, adhesives, and leather surface processing[26, 27].

1.3 Dynamic self-assembly

First, the hydrolyzed silicon source, surfactant, and co-structure directing agent form clusters that cluster together to form an organic/inorganic hybrid. The entire hybrid is relatively soft. Therefore, under the action of surface tension, it will spontaneously form a spherical structure, and with the progress of the reaction, a synthetic system in the range of pH = 8.8-6.4, spherical silica-encapsulated surfactant micelles inside spherical hybrids, SCM) continues to adjust spontaneously, adjusting to reduce the free energy of the surface of the micelle arrangement as the driving force, that is, the SCM free energy is reduced.

The self-adjusting mechanism is probably a common phenomenon in the preparation of mesoporous materials by self-assembly of supramolecular templates, but it is difficult to detect and track the self-adjusting process of cationic surfactants and non-ionic surfactants in synthetic materials. The organic/inorganic hybrids formed by the anionic surfactant-silicon source have a slower cure rate and allow sufficient time for self-regulation. The external morphology of the organic/inorganic hybrids during the self-adjustment process has a great influence on the formation of internal mesostructures. This hybrid with a certain morphology then undergoes self-adjustment to obtain a novel ordered mesostructure will be There are important potential applications for the preparation of new materials. In addition, the material of the radiation hole structure obtained by the self-adjustment process is more conducive to the diffusion of the substance into the sphere, which will have certain applications in heterogeneous catalysis, drug encapsulation and transmission.

1.4 Composite template

Composite template process: In this process, after calcination or chemical treatment, the hard template is removed to form the hollow part of the microspheres, and the soft template is removed so that the surface of the microspheres forms micropores. The hard-templating agent is uniformly dispersed into a composite system mixed with a soft template and a silicon source to prepare hollow nanoporous silica microspheres. G. S. Zhu et al.[28] prepared a microporous silica hollow sphere by accumulating a surfactant and a silicon source on the surface of negatively charged polystyrene PS microspheres under strong alkaline conditions (pH>12). The reaction mechanism is that positively charged surfactant micelles are attracted to the surface of negatively charged PS microspheres by electrostatic attraction. At the same time, the silicon source precursors self-assemble on the surface to form PS microspheres. /Surfactant-silica core-shell composite structure. The type and physical properties of the surfactant determine the distribution and size of the micropores in the hollow sphere. The size of the PS microsphere determines the size of the hollow sphere. The specific surface area of the hollow silica microspheres prepared in the experiment was 690 to 1830 m^2/g, the pore volume was 0.36 to 1.1 cm^3/g, and the pore size was 1 to 2 nm. D. BECKWI TH et al[29] also synthesized hollow microspheres using a hard and soft composite template.

In this process, surfactants with hydrophilic and hydrophobic groups, such as Sar-Na, increase to a certain concentration in a water solvent, form rod-like micelles, and are automatically arranged in a regular pattern to form a so-called "liquid crystal" structure. The hydrophilic group is oriented toward the water, while the hydrophobic group is concentrated inside. When the silicon source precursor is added, the silicate ions are bound to the charged ions of the surfactant through the electrostatic interaction, and adhere to the surface of the surfactant micelle, and simultaneously precipitate under certain reaction conditions. Under certain reaction conditions, precipitation occurs simultaneously. The product is washed, centrifuged, dried and calcined to remove the surfactant, leaving the framework silicate of mesoporous silica material.

Chapter 2　Experimental chemicals and instruments

2.1 Experimental chemicals

Reagent	Purity	Manufacturer
Styrene	AR	Shanghai Macklin Biochemical Co., Ltd.
Methacrylic acid	99%	Shanghai Macklin Biochemical Co., Ltd.
Ammonium persulfate	98.5 %	Shanghai Macklin Biochemical Co., Ltd.
N-Lauroylsarcosine sodium salt	98 %	Shanghai Macklin Biochemical Co., Ltd.
Tetraethylorthosilicate (TEOS)	SiO2>28.0 %	Tianjin Damao chemical Co., Ltd.
(3-Aminopropyl)triethoxysilane) (APES)	98 %	Shanghai Macklin Biochemical Co., Ltd.
(3-Aminopropyl)trimethoxysilane) (APMS)	97 %	Shanghai Macklin Biochemical Co., Ltd.
Methanol	AR	Tian in Fuyu Fine Chemical Co., Ltdj

2.2 Experimental instruments

Instrument	Specification	Manufacturer
Electric magnetic stirrer	78-1	Changzhou Boyuan Instrument Plant
Electronic balance	BT25S	Beiting Saiduolisi Instrument Co., Ltd.
Constant temperature drying oven	SX_2-2.5-10A	Shaoxing Shangyu Daoxu Analysis Instrument Factory

Supercentrifuge	GL-20G-II	Shanghai Anting Scientific Instrument Factory
Muffle furnace	FX-202-0	Shanghai Shuli Instrument Factory
Ultrasonic machine	JP-009	Skymen Cleaning Equipment Shenzhen Co., Ltd.
PH meter	PHS-3C	Hangzhou magnetic analysis instrument factory

2.3 Test instruments

Transmission electron microscope (TEM) observations were performed on a JEOL JEM-1400 TEM microscope and worked at 100 kV;

Nitrogen sorption and desorption isotherms were measured on a Tristar II 3020 sorption analyzer at a temperature of 77K. The specific surface area was calculated by BET (Brunauer-Emmett-Teller) method. The pore size distribution was determined by the adsorption branch using BJH (Barett-Joyner-Halenda) method to determine the total pore volume, p / p0 was 0.99;

Dynamic Light Scattering (DLS) measurements were performed on a Mastersizer A1 POL, which can be used to observe the particle size distribution and the sample powder was dissolved in water before measurement

Chapter 3   Experimental procedures

3.1 The synthesis of St-co-MAA copolymer spheres

Prepare a 10% NaOH solution and use it to wash styrene twice to remove a small amount of hydroquinone inhibitor from the purchased styrene to prevent it from

greatly affecting the polymerization process and the quality of the product [21.22]. The alkali-washed styrene is washed with ultrapure water to neutrality. 5.0 g of styrene and 0.75 g (0 g,1.00 g,1,5 g respectively) of α-methacrylic acid were weighed and mixed in advance and added it to a 250 mL three-necked flask together with 50 mL of deionized distilled water. An experimental device was set up, and the temperature of the constant temperature water bath was first set at 60℃. A condensation tube was installed on the side mouth of the three-necked bottle, and tap water was circulated to prevent gelation due to the evaporative solution during the reaction. On the other side of the three-necked flask, connected to a nitrogen tank, use a white latex tube to open the N_2 and insert the tube head under the liquid surface. Pass nitrogen and protect for one hour. Then, the temperature-controlled magnetic stirrer was set to a temperature of 70°C., heated to 70°C, stabilized for 10 minutes, and stirred at 500 rpm, so that the styrene monomer was sufficiently dispersed into the reaction system to form a homogeneous system. Using a needle, add 0.0378 g of potassium persulfate (APS) and 5 mL of deionized distilled water with a mixed initiator and react under N_2 protection for 5 hours. After suction filtration, the bulk material was removed, followed by centrifugation, washing with water, drying at 50 ℃, and standby.

3.2 The synthesis of hollow mesoporous silica

All chemicals are commercially available and were used as received. In a typical synthesis, 0.05 g Sar-Na was completely dissolved in 5 mL deionized water under stirring at room temperature. Then 0.05 g Polystyrene and 0.1 M HCl solution was added to the surfactant solution under vigorous stirring. Immediately the solution became a milky emulsion. The emulsion was vigorously stirred for 30 min at room temperature. Next a 250 μL mixture of 1.40 g TEOS, 0.24 g APES was added to the milky emulsion under vigorous stirring. The final molar ratio of the reactants was $100H_2O:0.04Sar-Na:0.28 TEOS:0.048 APMS$. After stirring for 1 h, the mixture was left in room temperature for 48 h. The white precipitate was filtered, washed with deionized water, and dried at 80 ℃. The surfactants were removed by calcination in air at 550 ℃ for 6 h. The experiments with different amount of HCl were carried out under similar conditions, but the HCl was put in 200 μL, 300 μL, 400 μL, 500 μL respectively and all the products were filtered and dried.

Chapter 4   Result and discussions

4.1 SEM and TEM images

4.1.1 SEM of St-co-MAA copolymer spheres

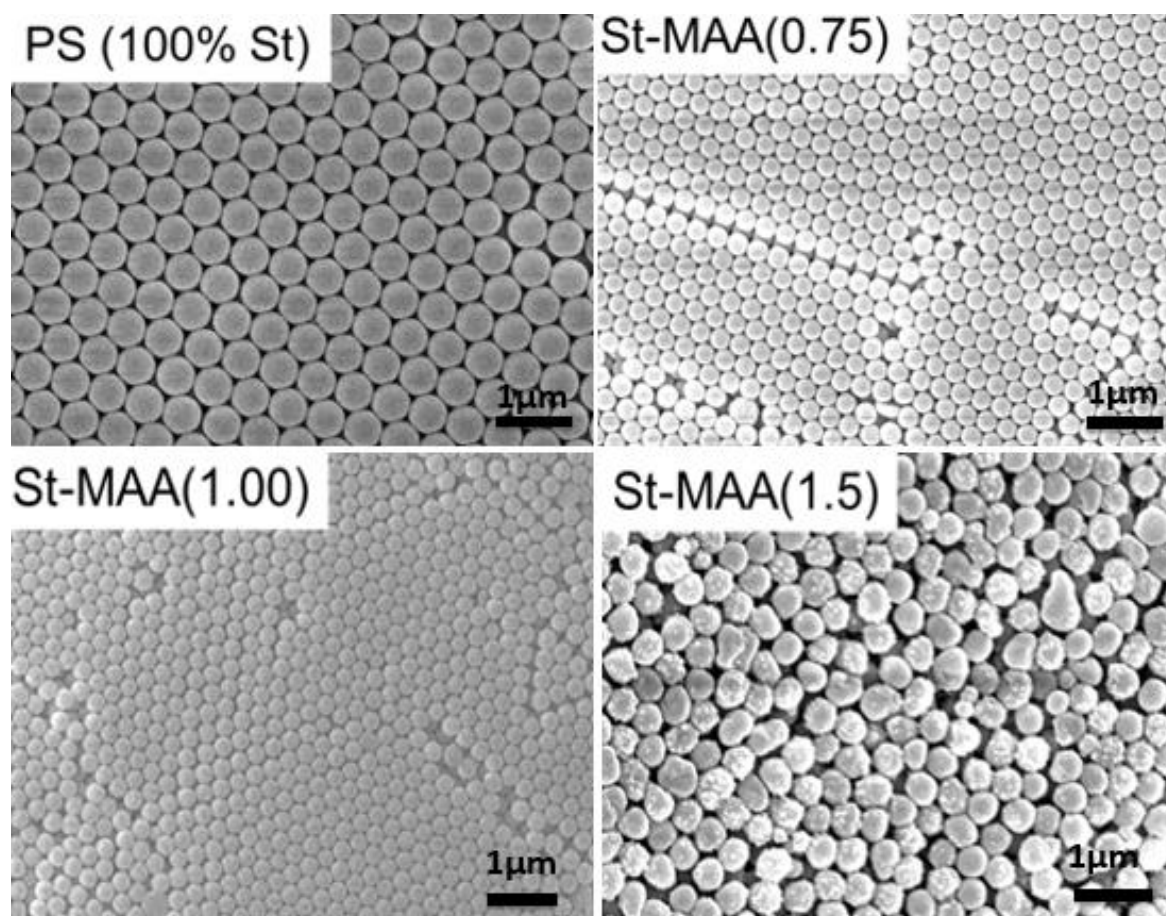

Figure 1: SEM images of St-co-MAA copolymer spheres with different ratio of St-MAA amounts. All the scale bar is 1 μm.

As shown in Figure 1, we can see clearly of the SEM images of the St-co-MAA copolymer spheres synthesized in no MAA, 0.75 g MAA, 1.0 g MAA, 1.5 g MAA respectively. In the first three SEM images (100%St, St-MAA (0.75), St-MAA (1.00)), we can observe that the microspheres have uniform size, good sphericity and smooth surface. Significantly, with no impurities on the surface and no cracks. And with the increase of the MAA ratio, the particle diameter of microspheres decreased. However,

in St-MAA (1.5), the microspheres become disordered and low sphericity.

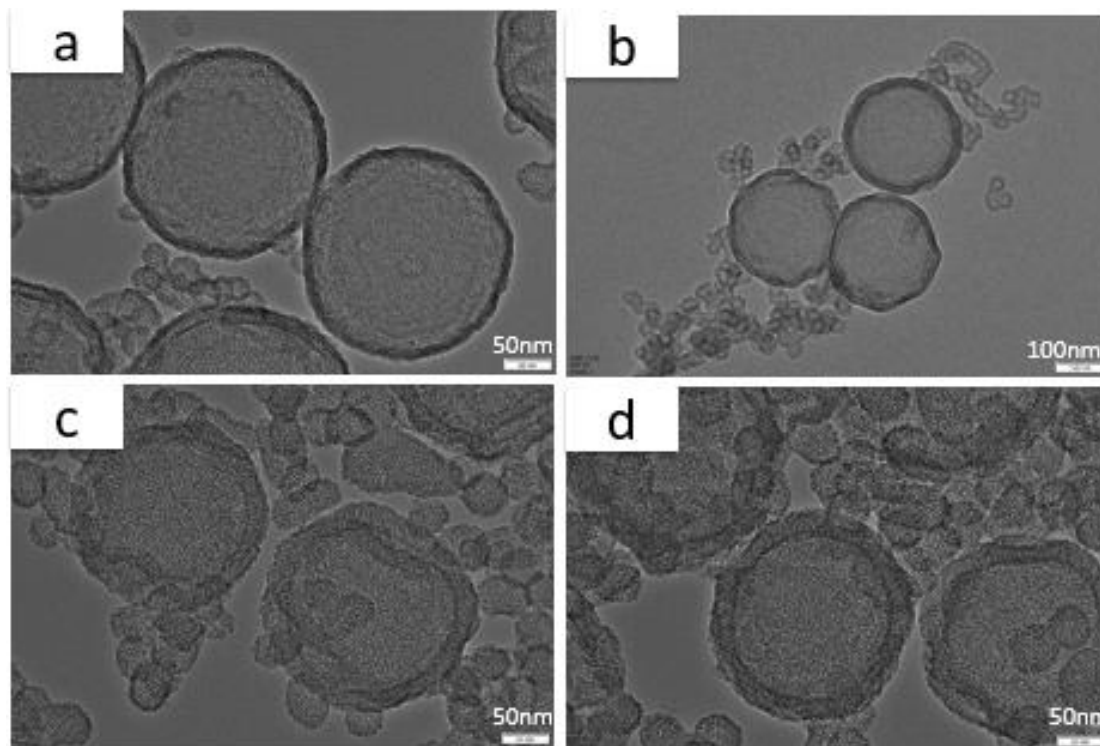## 4.1.2 TEM of hollow mesoporous silica

Figure 2: TEM imagines of synthesis of mesoporous silica hollow spheres with different amount of HCl (unit) a) 200 μL , b) 300 μL , c) 400 μL and d) 500 μL

Figure 2 shows a scanning electron microscope (TEM) image of the calcined product. From the image，we can see that all calcined samples are submicron spheres with a spherical mean diameter of 200 nm. Meanwhile, we can also find that the microsphere is hollow, and the order of the channel is low. Each microsphere has a layer of mesoporous silica (shell), and the thickness of the shell is uniform. Between 5-20 nm, the orientation of this layer of mesoporous silica is always perpendicular to the edge of the particle. It is worth noting that the morphology of the ball changes with the amount of hydrochloric acid. When the amount of hydrochloric acid is too low, the hollow spheres maintain a regular spherical shape. With the increase of hydrochloric acid, the surface of the hollow spheres become irregular. The shell has prominent protrusions and the wall of the beads is thickened. This may be due to the increase in the degree of hydrolysis of the silicate as the concentration of hydrochloric acid increases. The presence of some depressed hollow spheres may be due to the drying

and calcination of the sample.

We observed that as the amount of hydrochloric acid increases, the spherical wall thickness increases greatly and the specific surface area increases significantly. Therefore, the larger pore size may exist at the shell of the hollow mesoporous silica spheres, that is, the porosity is formed on the surface reaction. Also, as the amount of hydrochloric acid added gradually increases, the content of polymerized beads around the large ball also increases significantly.

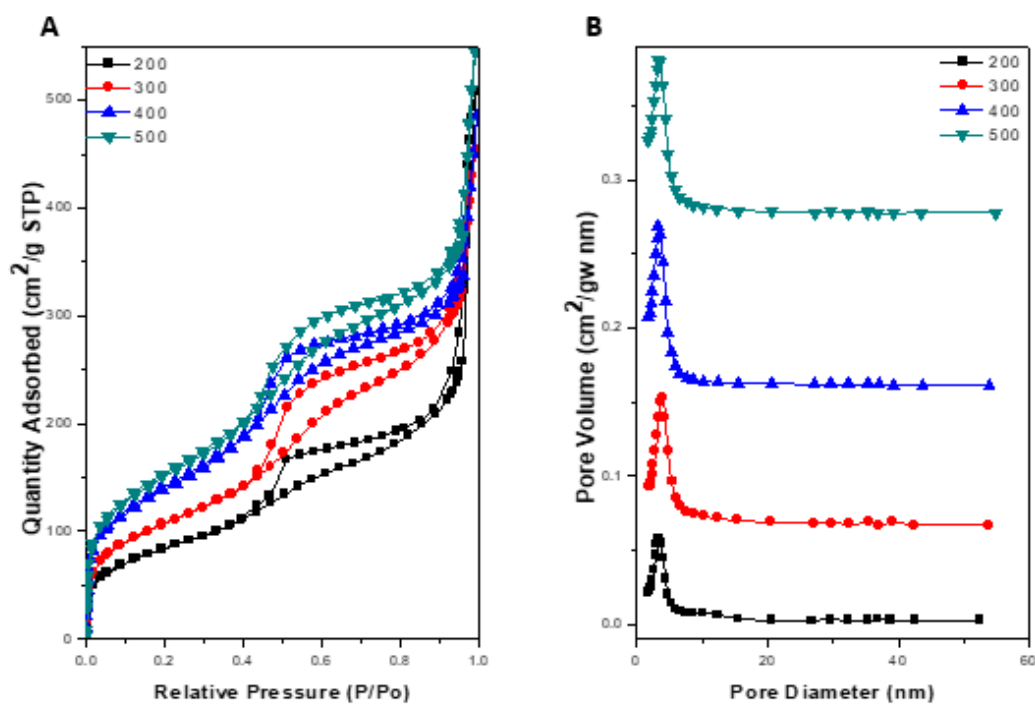## 4.2 Nitrogen adsorption-desorption

Figure 3. (A) Nitrogen adsorption-desorption isotherms and (B) pore size distribution curves of the mesoporous hollow spheres synthesized at different amount of HCl. (a)200 μL, (b) 300 μL, (c) 400 μL, (d) 500 μL.

Table 1. Structural parameters and pore properties of calcined products

Sample	BET surface area /m^2 ·g^{-1}	Mesopore Size /nm	Mesoporey Volume /cm^3 · g^{-1}
200	306	3.3	0.78
300	393	3.4	0.70
400	514	3.3	0.75
500	558	3.2	0.84

The nitrogen adsorption-desorption isotherms and pore size distribution curves of the mesoporous hollow spheres synthesized at different amount of hydrochloric acid are shown in Fig. 3. Because the Nitrogen adsorption desorption characterization curve has an obvious H1 hysteresis loop, it is a typical mesoporous channel which can be also proved in the pore size distribution curves. Nitrogen adsorption desorption characterization curve all exhibited type IV isotherms with two distinct adsorption steps at the relative pressure of 0.4-0.6, 0.90-0.99, respectively. The first at a relative pressure of 0.4–0.6 correspond to the relatively narrow peaks at about 3 nm in the pore size distribution curves, which were the cage-like pore size of the mesopores. We can also find that the pore size of mesopores has nothing to do with the amount of hydrochloric acid. With the increase of the amount of hydrochloric acid, the pore size of mesopores remains at about 3.3 nm. The second adsorption step, where relative pressure $p/p0 = 0.95–0.99$, was due to the voids of the aggregated nanoparticles or larger secondary nanopores. But the pore size exceeds the detection range of the nitrogen adsorption-desorption method, which we can see it from the TEM images. The textural parameters such as specific surface area, pore volume and pore size are given in Table 1. We can conclude that as the amount of hydrochloric acid increases,

the specific surface area of mesoporous silica continues to increase, when the amount of hydrochloric acid reaches 500 μL, the specific surface area reaches the maximum ($558 \text{ m}^2 \cdot \text{g}^{-1}$). That is because the role of hydrochloric acid is to act as a catalyst. With the increase of the amount of hydrochloric acid, it can promote the hydrolysis of silicate to generate more silicate ions. Second, it provides intermediate transitional ions Cl^- for the reaction system, and it promote the polymerization of silicate ions. Therefore, the larger pore size exists in the surface pores of mesoporous silica hollow spheres, the thickness of the spherical wall increases significantly, so the specific surface area increases significantly. We also found that the pore size of mesoporous silica hollow spheres with different content of hydrochloric acid is basically the same, which proves that the amount of hydrochloric acid has no effect on the pore size.

Chapter 5   Conclusions

In a conclusion, a new mesoporous silica hollow spheres with complex morphology, which contain a wormhole like mesoporous shell with mesostructured buds, has been fabricated by a composite-templating method. From the Figure 2, we can see that the hollow spheres maintain a regular spherical shape when the amount of hydrochloric acid is low, while the amount of the hydrochloric acid increased the surface of the hollow spheres become irregular. The shell has prominent protrusions and the wall of the beads is thickened. Also, from the Figure 3, the nitrogen absorption indicates that different amount of HCl won't affect the pore size but differs greatly in surface area. The hollow structure mesoporous silica which has prepared remains uniform size and good dispersibility. The hollow structure is left by the calcination of polystyrene microspheres. The hollow structure material will have a certain application in the fields of catalysis, drug encapsulation and transport.

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