



Preparation of mesoporous carbon monolith

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ABSTRACT

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In this paper, we introduce the preparation of three-dimensional ordered mesoporous carbon monolith using SNSs as templates. The key of this experiment was to prepare the uniform-sized silica nanospheres (SNSs). In our study, monodisperse SNSs were prepared by liquid phase method, which was based on Stöber method. The arrangement of SNSs into the cubic closed packed (ccp) structure was achieved simply by solvent evaporation, and they had high uniformity of size.

The size of SNSs was roughly analyzed by dynamic light scattering (DLS). It proved that SNSs 14 nm, 40 nm, 60 nm and 80 nm in size have been synthesized successfully. By changing the size of the sphere, the sizes of the pores between particles have been well adjusted, so it was beneficial to adjust the sizes of carbon materials subsequently. The fabrication process of carbon monolith was as follows, carbon precursors were filled into the voids of SNSs assembled into three-dimensional structure by incipient-wetness technique, and then the carbon monolith were obtained by carbonation in high temperature and removal of silica templates. The size and morphology of mesoporous carbon monolith were analyzed by scanning electron microscope (SEM). The specific surface area, pore volume and pore size of carbon monolith were characterized by N₂ adsorption-desorption. In addition, the application of

carbon materials mainly focused on the adsorption for volatile organic compounds (VOCs) and as battery electrode.

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Key words: three-dimensionally ordered carbon materials; silica nanospheres
seed regrowth: Incipient-wetness; VOCs; Battery electrode

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GLOSSARY or ABBREVIATIONS AND TERMS (choose one or other)

SNSs	silica nanospheres
ccp	cubic closed packed
DLS	dynamic light scattering
SEM	scanning electron microscope
VOCs	volatile organic compounds
TEOS	tetraethoxysilane

1 INTRODUCTION

1.1 The Mesoporous Carbon Materials

The porous material refers to kind of material having the large specific surface area and the different pore structures. According to the provisions of the International Union of Pure and Applied Chemistry (IUPAC), the pore size of the porous material can be divided into three groups: microporous material with pore diameter of less than 2 nm, and macroporous material with pore diameter of more than 50 nm; and the pore diameter between the two is mesoporous material¹. Porous materials include porous carbon, silicon and metal materials. In this paper, the synthesis of three-dimensionally ordered porous carbons using SNSs as templates and the preparation of SNSs with different sizes are introduced.

Porous carbon materials refer to carbon materials with different pore structures, such as traditional activated carbon, super activated carbon, activated carbon microspheres, carbon nanotubes, activated carbon fibers, carbon molecular sieves, etc². Well-ordered carbon material had a great number of good qualities, including high specific surface area, abundant porous structure, adjustable and uniform particles size, chemical inertness and pretty thermal stability. So it has wide applications in adsorption-desorption, catalyst and catalyst carrier, electrodes for fuel cells. For example, it can be applied to adsorbing heavy metal ions, gas capture and desalination of sea water. This paper studied adsorption propertiees of carbon materials, primarily tested the performence in VOCs adsorption, such as dichloromethane, toluene and n-hexane. The other important application paid attention to battery electrode.

1.2 The Synthesis Methods of Mesoporous Carbon Materials

There are carbonation, physical-chemical activation, organic gel and template methods³ to synthesize porous carbon. The pore structure of carbon materials obtained by carbonation and activation is difficult to control⁴. The equipment needed by organic gel method is more complex and expensive, so it is not easy to be used in industrial production⁵. Relatively speaking, the template method can make full use of the structural guidance of the template, and the controllable synthesis of the material can be carried out by changing the size, shape and the order of the pores, or by adjusting the assembly mode of the template, so it is likely to control voids size successfully. For all above reasons, template method becomes the most potential, commonly synthesis method. Therefore, the template method is used to synthesize porous carbon monolith in this paper.

Template method is first used in the preparation of organic materials. In simple term, it selects the material with specific pore structure as a template, the target material is imported into voids and reaction is initiated. Taking advantage of the limited field effect of the template, it is able to control the physical or chemical reaction in the process, so as to prepare a new type of material with controllable micro structure and macro structure. According to the characteristics of template, template methods can be divided into hard template method and soft template method⁶. The soft template method uses surfactants as templates, and the porous structure is formed by organic-organic self-assembly between the template and carbon precursor, and then the porous carbon material is obtained by removing the template⁷. The porous carbon material assembled by soft template method has limited pore size and can not produce carbon material with large pore size. Moreover, the soft template is unstable, so the preparation process is difficult.

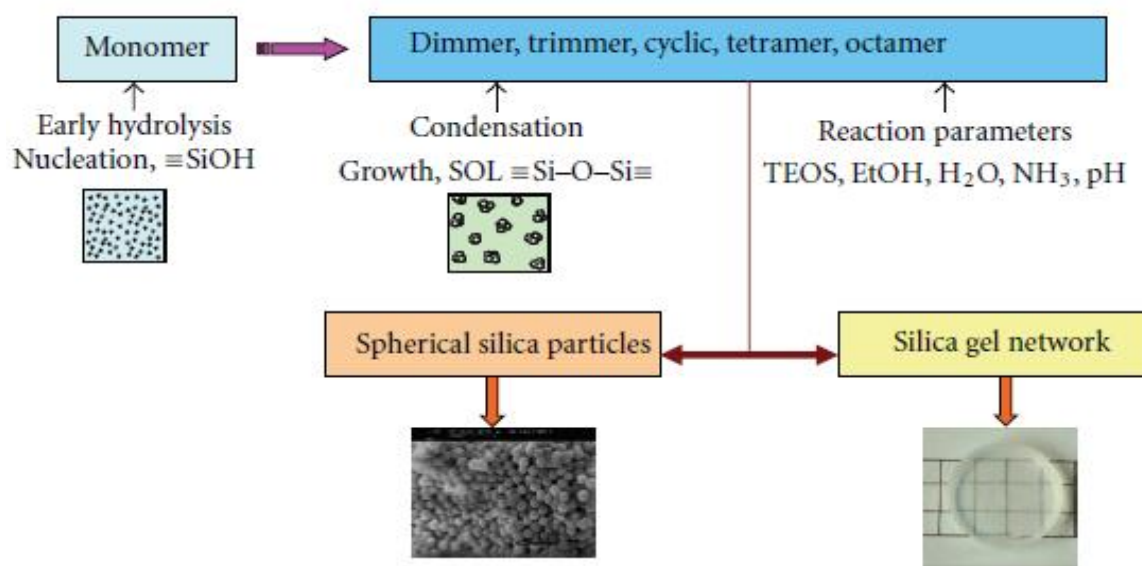
Hard template method is also called inorganic template method, mainly uses porous material as template, such as silica gel, porous glass, spherical silicon oxide in mesoporous shell, cellular silicon-aluminum sponge, etc. The target material is filled into the voids by liquid phase impregnation or vapor deposition, and then the mixture is carbonized at high temperature to remove template. Finally, the carbon material which is similar to the network structure is obtained².

The advantage of the hard template method is that the template is porous material, and the carbon precursor is filled into the voids of the template through physical action mainly. So the porous carbon material, which is the reverse structure of silica template, can be obtained after removal of the template. In synthesis process, the controllability can be realized by changing the spheres' size, shape and structure order of the template. The pore size range of the carbon material is wide (10 nm-100 nm), so the product has strong applicability. Another thing worth noting is that hard template method has many kinds of templates, wide carbon source selectivity and cheaper synthesis raw materials, so it can be used in industrial production.

The requirements of hard template method are as follows: firstly, the template itself should have uniform pore structure and good thermal stability; Secondly, the molecule size of selected carbon precursor should match the pore size of the template, and must have a high carbon yield, such as sucrose, furfuryl alcohol, etc, so as to ensure the filling of the template's channel; Finally, the interaction force between template and carbon precursor should not be too large, in order to avoid the destruction of the structure of the carbon material when the template is removed.

1.3 Synthesis Methods for SNSs

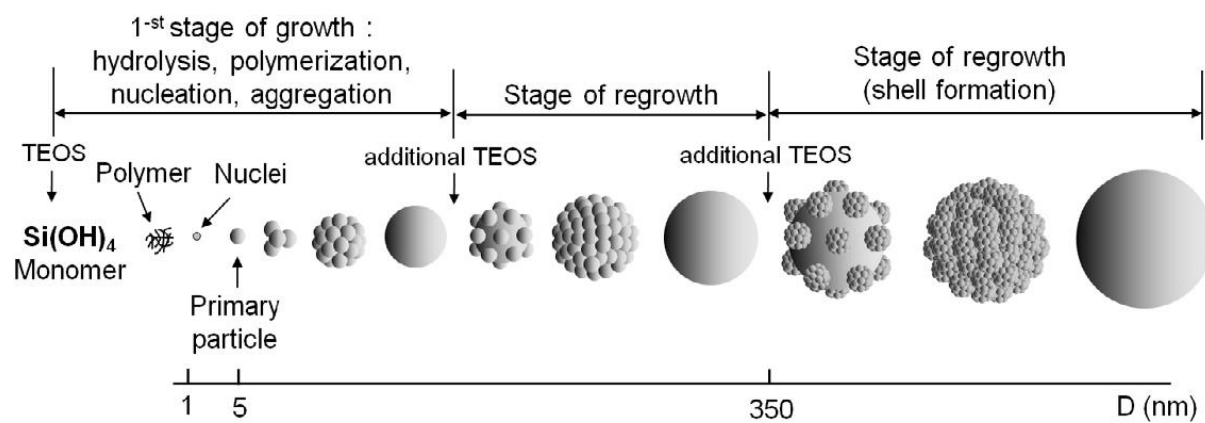
Because we selected well-ordered porous SNSs as templet, so it was vital to prepare uniform-sized SNSs. There are many preparation methods for SNSs with high uniformity in size, including sol-gel (Scheme1), precipitation, microemulsion method⁸. Sol-gel process is an important method to prepare monodisperse SNSs. In this method, metal alcohols or inorganic salts are used as precursors, and the required materials are obtained after hydrolysis, polycondensation and some post-treatments such as aging and drying⁹. Stöber found that monodisperse SNSs can be formed by using ammonia as catalyst in tetraethoxysilane (TEOS) hydrolysis¹⁰. This method was referred to synthesize well-distributed SNSs in my paper. TEOS conducted hydrolysis and condensation reactions in an emulsion system containing TEOS, water and L-arg under weakly alkaline conditions, then the SNSs were synthesized. After the reaction, SNSs with high uniformity in size were stably dispersed in homogeneous solutions without any deposition. The arrangement of SNSs into the well-ordered structure was achieved simply by solvent evaporation. This route for producing mesoporous materials has been called as “hard-template method” mechanism¹¹. So SNSs can be categorized into well-ordered mesoporous silicas because they have three-dimensional, interparticle voids with high uniformity of size.



Scheme 1. Schematic silica formation by sol gel method ¹²

1.4 Seed Regrowth

Because the diversification of SNSs size has greatly expanded its application fields, so many scholars paid attention to the accurate control of its size. SNSs with different size was prepared by seed regrowth¹³ in this paper, so the diversification of interparticle voids was increased. Seed regrowth technique is based on the further growth of preformed silica particles to inhibit the formation of new particles by adding silicon precursors such as TEOS. The TEOS introduced in the regrowth stage only contributed to the growth of seeds, but did not form new silica particles. The size of the final silica particles is controlled by adjusting the amount of TEOS in the seeds dispersion and the number of the seed¹⁴. The schematic drawing of the seed regrowth process is shown in Scheme 2.

Scheme 2. Particle growth during multistage growth¹⁵

2 SILICA NANOSPHERES

2.1 Experimental Chemicals and Instruments

Please start writing here. (If you only want to remove the example table, click on the table and then select from the top menu Layout -> Delete Table. If you bring a ready table to the document, use the function Paste Special.)

TABLE 1. Chemicals for prepare SNSs

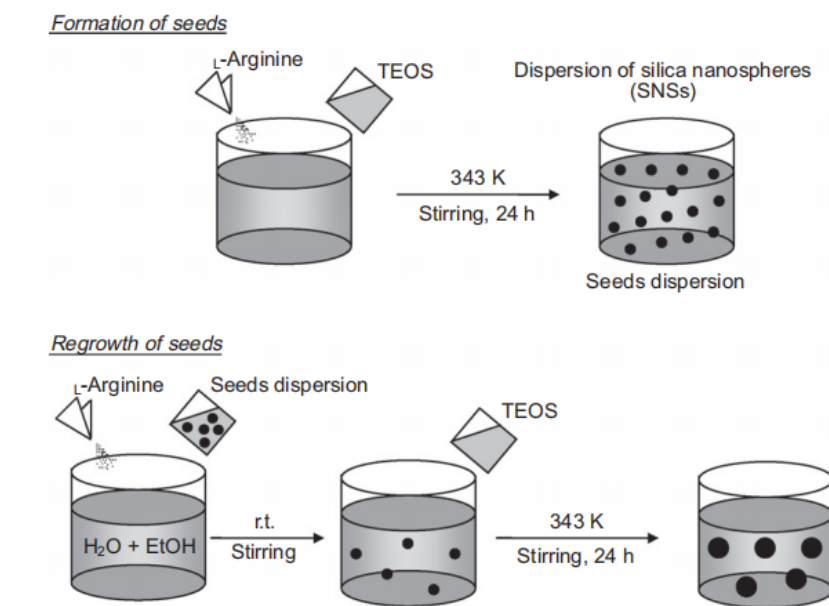
Reagent	Purity	Manufacturer
L-Arginine	≥ 98% (TLC)	SIGMA-ALDRICH Co., Ltd.
Tetraethyl orthosilicate (TEOS)	AR (SiO ₂ ≥ 28.0%)	Tianjin Damao Chemical Co., Ltd.
Ethanol	AR (≥ 99.7%)	Tianjin Fuyu Fine Chemical Co., Ltd.

TABLE 2. Instruments for prepare SNSs.

Instrument	Specification	Manufacturer
Thermostatic magnetic stirrer	C-MAG HS 7C S025	Aika Instrument Equipment Co., Ltd.
Electronic balance	SQP	Sartorius Scientific Instruments (Beijing) Co., Ltd.
Constant temperature drying oven	202-00A	Shanghai Yetuo Scientific Instrument Co., Ltd.
Electric box resistance Furnace	SX2.5-10	Shanghai Shuli Instrument Co., Ltd.

2.2 Experimental Procedures

Experiments were mainly completed in two steps, including the synthesis of the seed dispersion solution (SNS 14 nm in size), and the subsequent seed regrowth process, to obtain SNSs with all sizes. The whole processes are shown in Scheme 316. In our method, first, we added an appropriate portion of the seeds dispersion to the solution containing L-arg, water and EtOH. Then TEOS was added to the solution. Our seed regrowth method mainly change the ratio of the numbers of TEOS in seeds dispersion to added TEOS, the total amount of TEOS kept constant at the same time.



PICTURE 1. Schematic drawings of the formation of silica nanospheres

2.2.1 Synthesis of Seeds Solution

Silica nanospheres seeds were synthesized by a simple liquid phase method. TEOS was as the silica source in this method. First of all, L- arginine (0.174 g, 1 mmol), the basic amino acid, was dissolved into distilled water (174 g, 9.7 mol). Then it was allow to stir for some time to dissolve L- arg completely. Then TEOS (10.41 g, 50 mmol) was added to the above solution and start to stir for 6 h at 60 oC with 500 rpm. At beginning the system had two phases, oil phase which included unhydrolyzed TEOS and water phase containing L-arg. After 10 h, the seeds dispersion were formed. The dispersion solutions were kept in a plastic bottle for later use. Another part of the dispersion solutions were dried in 353 K drying oven, then calcined in 773 K muffle furnace, then the solid fully ground into powders by agate mortar and preserved for DLS test.

The DLS image of the shows that monodisperse SNS 14 nm in size were formed (Fig. 1). The SNS monodispersion containing 14 nm particles was used as seeds.

2.2.2 Synthesis of Seeds Solution (SNSs 14 nm in size)

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The DLS image of the shows that monodisperse SNS 14 nm in size were formed (Fig. 1). The SNS monodispersion containing 14 nm particles was used as seeds.

2.2.3 Synthesis of SNSs with Dfferent Sizes (40nm , 60 nm and 80 nm)

Ryota Watanabe ¹⁶ once reported the relationship between amount of TEOS and size of final R-SNSs. According to the previous study on the seed regrowth technique based on the Stober method, the size of final product (S product) can be controlled by the following equation.

$$S_{seed}^3 / S_{product}^3 = M_{TEOS, seed} / M_{TEOS, total} = m$$

We mainly referred to above equation, R-SNSs 40 nm, 60 nm, 80 nm in size were synthesized in our study. But the accurate amount of samples were not same completely because of different experimental conditions. The accurate amount of seeds dispersion and MTEOS is listed in Table 3.

Table 3. Amount of seeds dispersion and M_{TEOS}

	Size/nm	Water/g	EtOH/g	L-arg/g	Seed/g	TEOS/g
Sample1	14	174	-	0.174	-	10.41
Sample2	40	49.105	125.541	0.174	4.063	4.979
Sample3	60	49.105	125.541	0.174	1.184	5.183
Sample4	80	49.105	125.541	0.174	0.480	5.180

The subsequent addition of TEOS only plays an important role in the recovery and growth of seeds, but does not form new silica particles. By keeping the total amount of TEOS unchanged, the synthesis of R-SNSs with different sizes were realized by changing the proportion of TEOS in the seeds to the amount of TEOS added.

The monodisperse R-SNSs over 150 nm in size were successfully prepared by changing the compositions of TEOS, L-arg, H₂O and EtOH with m varied. But we did not try to prepare R-SNSs over 150 nm in size, so this theory was not proved.

In weakly alkaline solution, the proper amount of seeds dispersion (SNS 14 nm in size) were added into the solution comprising by L-arg, water and ethanol, and then a certain proportion of TEOS was added. The whole system was heated for 6 h at 334 K with 500 rpm.

A small amount of liquid was taken for DLS test to obtain the size of the sample (Fig 1-2). Other samples were dried in 353 K constant temperature drying oven, incinerated in 773 K muffle furnace, ground in a agate mortar. Finally white powders of R-SNSs were obtained after solvent evaporation.

2.3 Characterization and Analysis

Dynamic Light Scattering (DLS) were performed on Mastersizer A1 POL, which can be used to observe particle's size, the particle size distribution was represented by the intensity distribution (Fig. 1- 2).

Nitrogen adsorption and desorption isotherms were conducted on a Tristar II 3020 sorption analyzer at 77 K. Specific surface area (Fig. 3) was calculated by BET (Brunauer- Emmett-Teller) method, the pore-size distribution (Fig. 4) was calculated from the adsorption branch using BJH (Barett-Joyner-Halenda) method and total pore volume was obtained at p/p_0 of 0.99, The sample pretreatment was purged with nitrogen at 200 °C for 5 h and then started to adsorb in liquid nitrogen at 77 K.

2.3.1 DLS Analysis

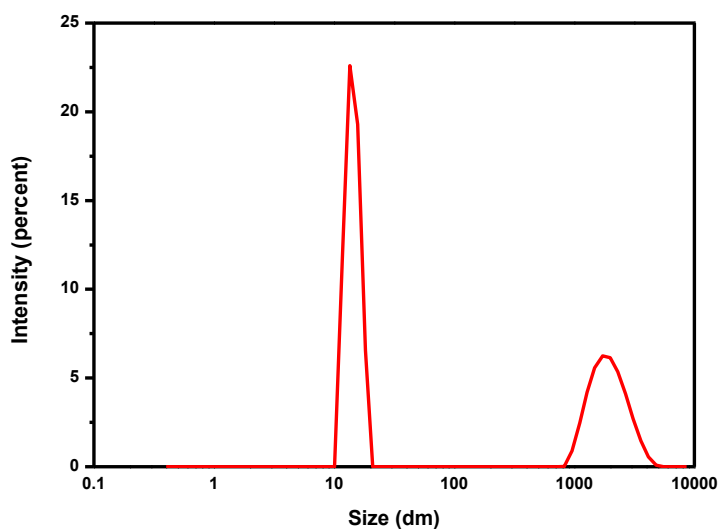


FIGURE 1. DLS curve of SNS 14 nm in size.

From the dynamic light scattering diagram, we can find that the average diameter of the sample particles was mostly 14.38 nm at the main peak position, which accounted for 60.2%. It is well known to all that there was certain error, because the size of samples was so small. Matter distributing above 1000 nm might be dust. So above DLS curves confirmed SNS 14 nm in size have been synthesized.

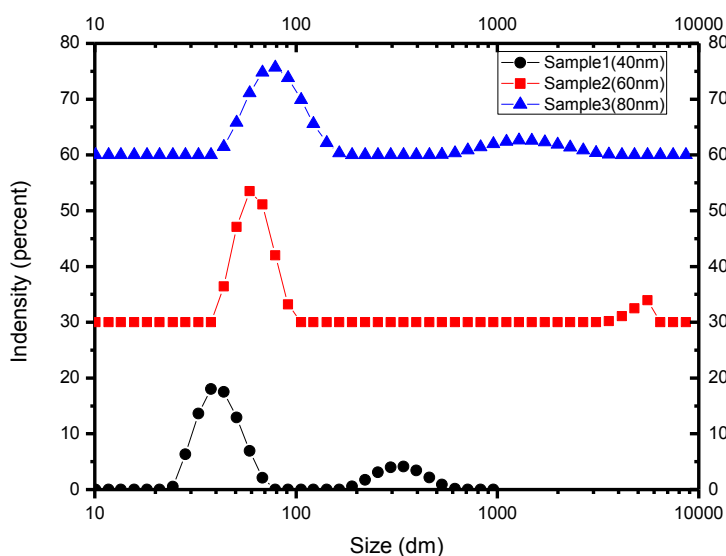


FIGURE 2. DLS curves of R-SNSs 40 nm, 60 nm, 80 nm in size.

From above figures, we could obtain information as follows: Black curve shown the sample1 is R-SNS 81.93 nm in average size, whose percent is 90.7% . R-SNS 59.01 nm in size was shown in red curve with 80.3% percent. Blue curve represented R-SNS 40.25 nm in size, which accounted for 67.2%.

By all figures, we can analyse sizes of R-SNSs dispersion roughly. So it was convincing that R-SNSs with different size were prepared by seed regrowth technique. Another thing we should considerate is that one peak proved the R-SNSs is monodisperse and they have high uniformity in size.

2.3.2 Nitrogen Adsorption-desorption

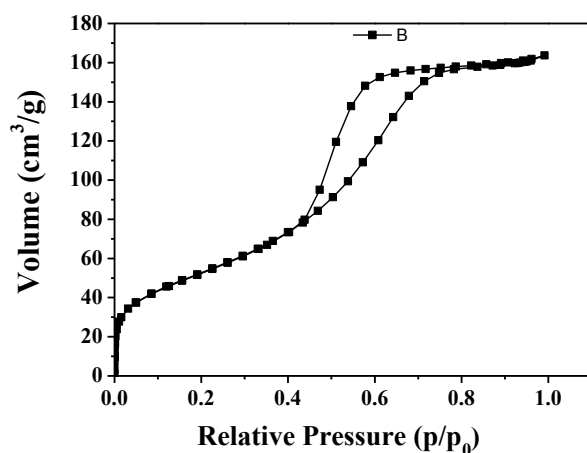


FIGURE 2. Nitrogen adsorption-desorption isotherms of SNS seed.

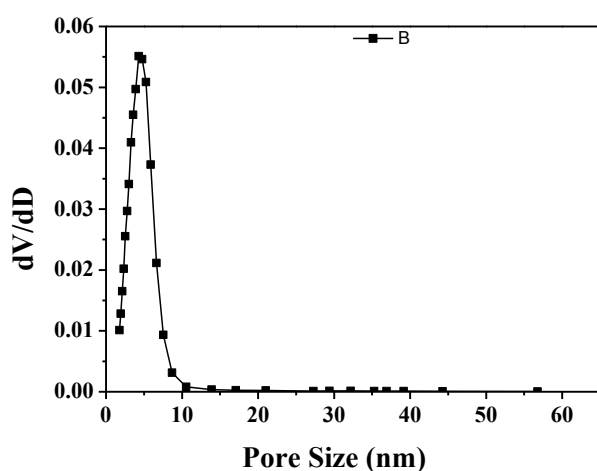


FIGURE 2. Pore size of SNS 14nm in size.

Nitrogen adsorption-desorption isotherms of SNS 14 nm in size are shown in Fig. 3. There were the type IV pattern with the so-called “bottle-neck type”. From Fig. 3, we could get following information: the BET surface area was 193 m²/g. The pore volume less than 220.60 nm diameter at P/P₀ = 0.99 was 0.25 cm³/g. The Fig. 4 shows the pore size of sample was 5.11 nm.

2.4 Synthesis Mechanism

2.4.1 Regrowth Mechanism

DLS analysis proved the following fact, In the process of seed regrowth, no matter how the amount of TEOS was changed and the reaction time was adjusted, the silica dispersion is uniform and stable. So we could draw a conclusion, TEOS added only contributed to seed regrowth, not to form new particles. We can explain this phenomenon as follows, The reaction systems of both formation and regrowth of the seeds were under weakly alkaline conditions; the hydrolysis rate of TEOS was not remarkably high but the condensation of silicate species would be very quick¹⁷. Note that a large number of reactive

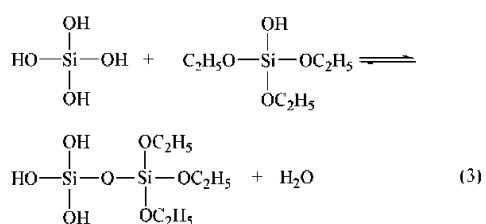
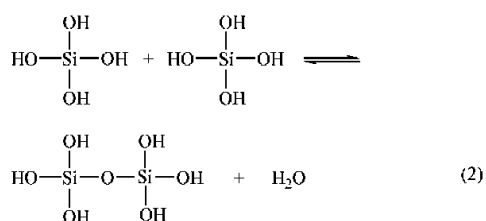
silanol groups are present on the surface of the seeds¹⁸. Therefore, under such conditions, it is possible that incremental silicate species are used for secondary growth of the seeds by condensation with surface silanol groups rather than for the formation of new silica particles. This growth process would be same with the monomer addition mechanism¹⁹. This is based on the fact that the particles grew until the equilibrium concentration was reached by adding the monomer to the surface of the parent particles.

2.4.2 Mechanism of SNSs Synthesis

Under alkaline condition, The hydrolysis and condensation of TEOS is divided into two steps²⁰.

First step: Hydrolysis

Second step: Condensation



In the first step, TEOS was hydrolyzed to form hydroxylated products and corresponding alcohols. In second step, condensation reaction took place between silicic acid and TEOS. In fact, the reaction of the first step and the second step was carried out at the same time, and the process was very complex, so it was almost impossible to describe the hydrolysis and

polycondensation process independently. The reaction products are sol particles of different sizes and structures.

3 MESOPOROUS CARBON MONOLITH

3.1 Experimental Chemicals and Instruments

Table 4. Chemical for prepare carbon monolith

chemicals	Purity	Manufacturer
Furfuryl alcohol	CP ($\geq 97\%$)	Shanghai Macklin Biochemical Co., Ltd.
Oxalic acid	AR ($\geq 99.5\%$)	Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.
Hydrofluoric acid (HF)	$\geq 40\%$	Laiyang Kangde Chemical Co., Ltd.

Table 5. Instruments for prepare carbon monolith

Instrument	Specification	Manufacturer
Constant temperature drying oven	202-00A	Shanghai Yetuo Scientific Instrument Co., Ltd.
Ultrasonic cleaning machine	JP-009	Shenzhen Jiemeng Cleaning Equipment Co., Ltd.
Electronic balance	SQP	Sartorius Scientific Instruments (Beijing) Co., Ltd.
Centrifuge	H1850	Changsha Xiangyi Centrifuge Instrument Co., Ltd.
Tubular resistance furnace	ZL-22011-2	Hefei Kejing Material Technology

3.2 Experimental Procedures

3.2.1 Preparation of Common Carbon Materials

In the carbonation process, silicon spheres of all sizes were used as templates, furfuryl alcohol was as carbon source and oxalic acid was as catalyst. 0.01 g oxalic acid was dissolved by 10 g furfuryl alcohol. Then the carbon precursor was filled into the voids of templates by incipient-wetness technique. After soaking completely, the SNSs/ furfuryl alcohol complex was heated in 373 K drying oven for 48 h, and then heated at 423 K for 8 h to polymerize furfuryl alcohol. Subsequently, the polymerized furfuryl alcohol was converted to carbon in the interparticle pores. The complex was carbonized in a tubular resistance furnace for 3 h at 1073 K. The above treatment will produce black

monolith (Fig. 5-6), and then at room temperature, 40% HF will be used to remove the silica templates, and after multiple washing, the final products (Fig. 9-10) would be obtained. In order to better cross-link, we added certain polyaniline in incipient-wetness process. Sample was shown in Picture Fig. 7-8.



FIGURE 5. Sample with silica template.

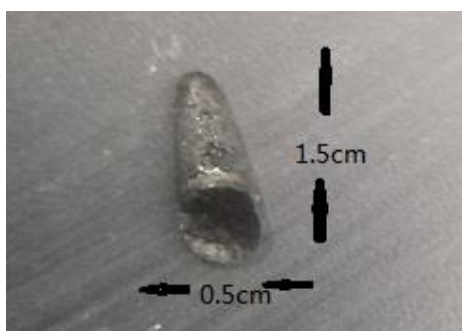


FIGURE 6. Sample with polyaniline.

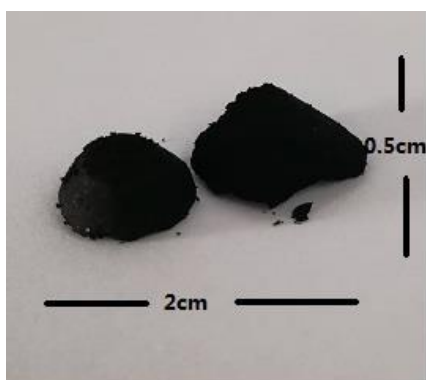


FIGURE 7. Sample without silica template.

3.2.2 Preparation of carbon Monolith with Pt

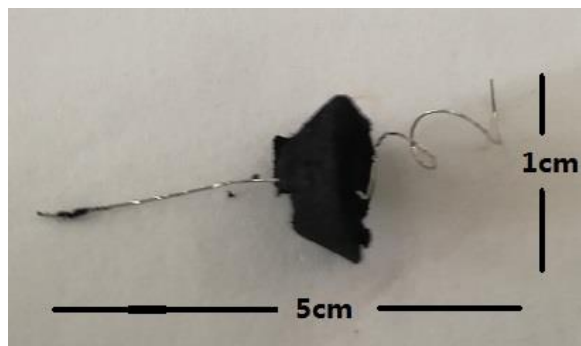


FIGURE 8. Carbon Monolith with Pt.

3.3 Characterization and Analysis

Field-emission scanning electron microscope (SEM) images were recorded on a JEOL JSM-7600F microscope at 5 KV. SEM images of carbon are shown in Fig. 13A-13B.

Nitrogen adsorption-desorption isotherms were conducted on a Tristar II 3020 sorption analyzer at 77 K. Specific surface area (Fig. 14) was calculated by BET (Brunauer- Emmett-Teller) method, the pore-size distribution (Fig. 15) was calculated from the adsorption branch using BJH (Barett-Joyner-Halenda) method and total pore volume was obtained at p/p_0 of 0.99. The sample pretreatment was purged with nitrogen at 200 °C for 5 h and then started to adsorb in liquid nitrogen at 77

3.3.1 SEM Image

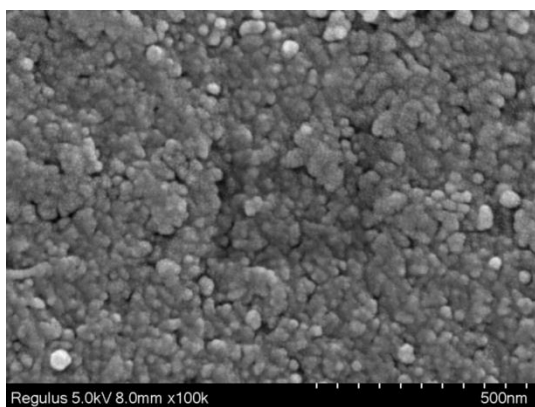


FIGURE 9. SEM of porous carbon.

As is shown in Fig. 13A-13B, we can see clearly that the SEM images of the porous carbon monolith. We can observe that the porous spheres have uniform size, good sphericity and smooth surface. The pores are uniform, close-packed and spherical, revealing the formation of a highly ordered porous carbon framework. Each of the spherical pores is also three-dimensional interconnected to neighboring pores through small holes, which were attributed to the contact points between closely-packed silica spheres.

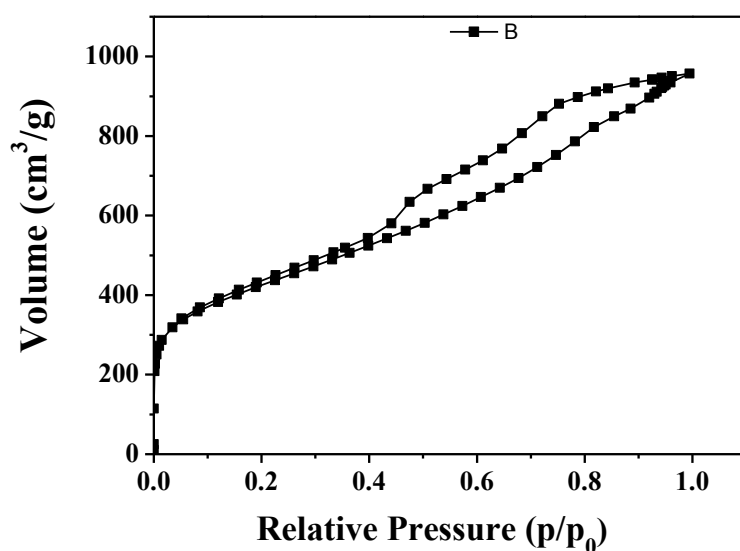


FIGURE 10. Nitrogen adsorption-desorption isotherms of carbon monolith.

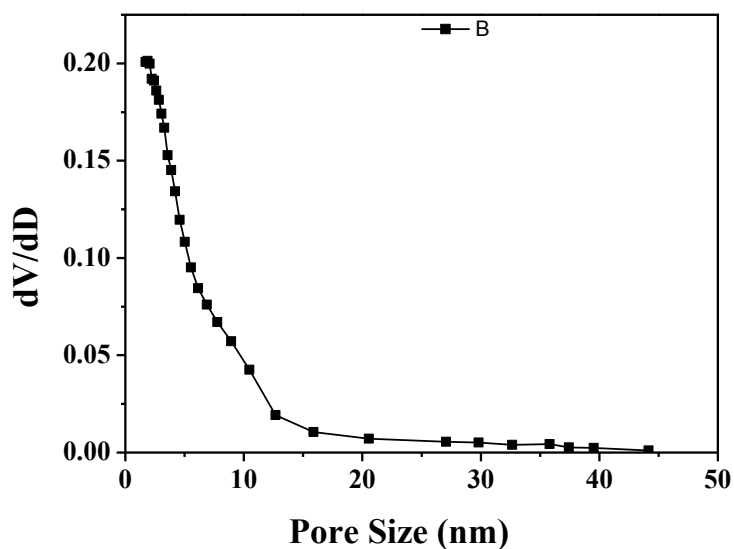


FIGURE 11. Pore size of carbon monolith.

Nitrogen adsorption-desorption isotherms of carbon monolith using SNS 14nm in size are shown in Fig. 14 and Fig. 15. We could get following information from Fig. 14, the BET surface area was 1,502 m²/g. The pore volume less than 355.77 nm diameter at P/Po = 0.99 was 1.48 cm³/g. The Fig. 15 indicates the pore size was 1.58 nm.

3.4 Applications of Mesoporous Carbon Monolith

The application test of carbon materials is mainly in the adsorption of volatile organic compounds (dichloromethane) and as electrodes.

3.4.1 Performance of Being Battery Electrode

We have assembled a simple water electrolysis device to test the performance of porous carbon monolith as electrode (Fig. 16). Porous carbon materials as anode and cathode was compared with common carbon rod (Fig. 17), then we

found that water electrolysis reaction was more intense when we use porous carbon as electrodes. Because carbon capacitor electrode having porous morphology and large surface area as a counter electrode, so large charge amount consumed by multiple redox pairs' cathodic materials was adequately compensated.

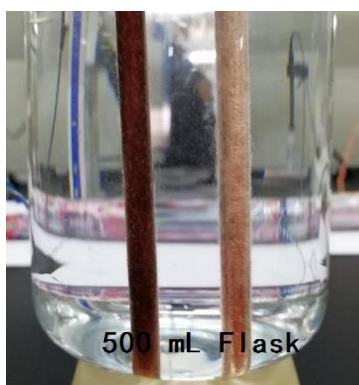


FIGURE 12. Common carbon as electrode.

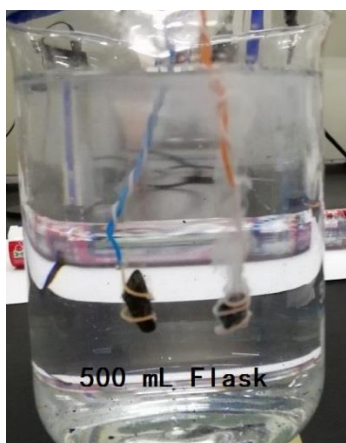


FIGURE 13 Mesoporous carbon as electrode.

3.4.2 Adsorption Property for Volatile Organic Compounds (VOCs)

Dichloromethane was chosen to test the adsorption performance. As is shown in Fig. 18, porous carbon capture ability could reach 76% at the temperature above the boiling point of CH_2Cl_2 (312.8 K). Compared with activated carbon, porous carbon had good adsorption ability. Uniform porous structure and less-hydrophilic surface were two important factors for a good adsorbent to capture VOCs, including dichloromethane, n-hexane and toluene

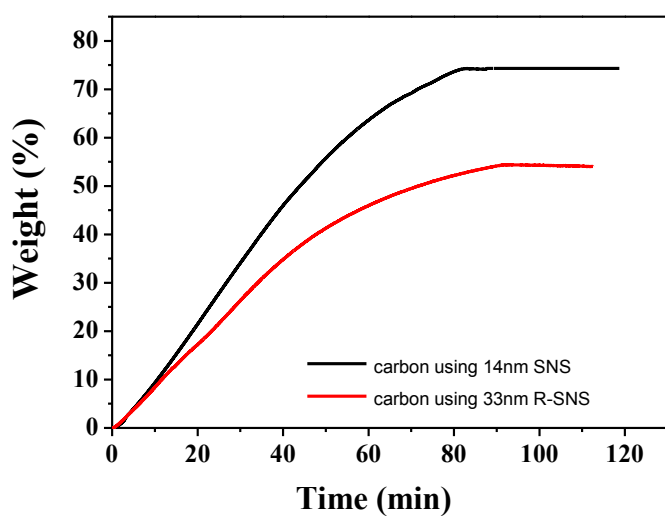


FIGURE 14 The adsorption for CH_2Cl_2 of carbon monolith

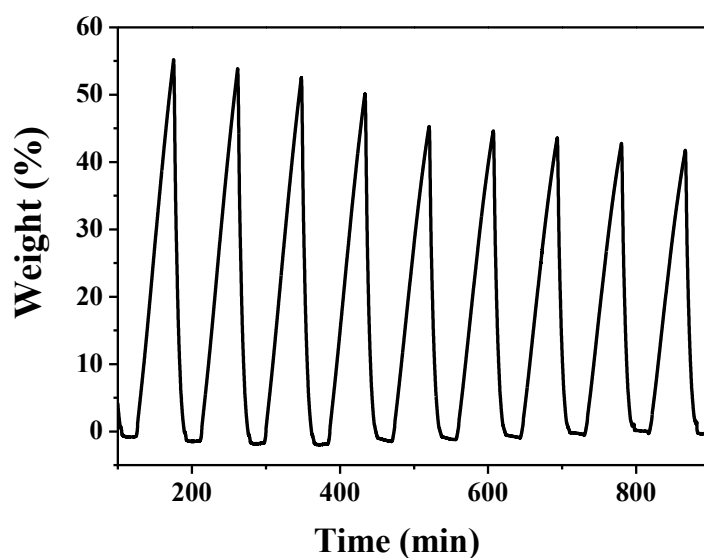


FIGURE 15. The adsorption for CH_2Cl_2 of carbon monolith in different Time.

Fig. 14 shows the typical adsorption images for VOCs of carbon monolith, indicating that carbon monolith, which was prepared by SNS in 14 nm size, could adsorb 74% CH_2Cl_2 , and carbon monolith, which was prepared by SNS in 33 nm size was also able to adsorb 52% CH_2Cl_2 . Activated carbon only adsorb 36% VOCs. So carbon monolith have excellent adsorption ability for VOCs. We could know the carbon monolith is stable in adsorption VOCs in different temperature from Fig. 15

4 DISCUSSION

In this paper, the preparation of porous carbon using silica as templates and the fabrication of SNSs 14 nm、40 nm、60 nm and 80 nm in size were reported. The application of carbon monolith focused on adsorption of VOC and battery electrode. Silica dispersion solution was prepared by liquid phase method. In this process, silica assembled into well-ordered silica nanospheres (SNSs) with uniformity in size. The analysis of DLS showed that the SNSs 14 nm、40 nm、60 nm and 80 nm in size were successfully controlled by seed regrowth technique. These works made good preparation for the production of three-dimensional ordered porous carbon monolith. The mechanism of the synthesis for SNSs dispersion and seed regrowth were also explained briefly. In this paper, porous carbon were synthesized by hard template method. Using SNSs, furfuryl alcohol and oxalic acid as template, carbon source and acid catalyst respectively, furfuryl alcohol and oxalic acid were filled into the interparticle gap of SNSs , and the complex were heated to polymerize furfuryl alcohol, and then the polymerized furfuryl alcohol were converted to carbon in the interparticle voids of SNSs. Finally, HF aqueous solution was used to remove silica template. In order to test the electrochemical application of carbon monolith, several carbon materials with Pt with polyaniline as crosslinker were also synthesized. Finally, N₂ Nitrogen adsorption-desorption isotherms proved that the carbon monolith had high specific surface area. The highest BET area could reach 1,502 m²/g. SEM image shown the porous carbon material had three - dimensional ordered morphology actually. The adsorption isotherms for CH₂Cl₂ showed that porous carbon monolith have good adsorption properties for volatile organic compounds. The electrode test of carbon monolith with Pt proved it has great advantage in electrochemical

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