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Progress in Preparation of Mesoporous/Nano Materials by Surfactant Template Method

Minghao Dong

School of Material Science and Engineering, Hubei University, China

Abstract

Mesoporous materials refer to a class of porous materials with a pore diameter between 2-50nm. They are characterized by extremely high specific surface area, regular and orderly pore structure, small size effect, quantum size effect and continuously adjustable pore size, etc., and are widely used in many fields. There are many methods to synthesize mesoporous materials, such as sol-gel method, microwave assisted technique, chemical etching technique and template method. One of the most common and widely used methods is the template method.The template method is a method in which the aggregate formed by the self-assembly of surfactant molecules is used as the template and the monomers are triggered to coalesce on the template to form an ordered porous material. It has become a common method to prepare mesoporous and nanomaterials by template method.In this paper, the application of five different types of template agents (cationic, anionic, non-ionic, mixed surfactant and polyelectrolyte - surfactant mesoporous complex) in the preparation of mesoporous materials by template method was introduced, and the latest research progress was reviewed. The different mechanisms and characteristics are also described. In the end, the future surfactant template method and template agent development prospects are summarized.

Keywords

Mesoporous materials; Template method; Template; Surfactant; Polyelectrolyte Surfactant Mesocrystalline complex.

1. Preface

Surfactant (Suface active Agent;Surfactant, SAA), is a kind of very important chemical handicrafts, is a kind of solution to join a small amount can significantly reduce the surface tension of the (usually water) or the interfacial tension of liquid-liquid and, in turn, change solution interface properties of the material, its wetting or viscous resistance, emulsification and demulsification, blister or defoaming, solubilization, dispersion, washing, antistatic and a series of physical and chemical action, in the early days more used for washing and textile industry, is now widely used in various industries in the field of fine chemical industry and even the life of the parties,Such as textile industry, mineral flotation, material molding, food processing and so on.Surfactant molecules are amphiphilic, with polar hydrophilic groups at one end and non-polar hydrophobic groups at the other.

According to the international Union of Pure and Applied Chemistry (IUPAC), mesoporous materials refer to porous materials with pore diameter between 2-50nm. Mesoporous materials are characterized by extremely high specific surface area, regular and orderly pore structure, narrow pore diameter distribution, and continuously adjustable pore size, etc., which make it play a role in adsorption and separation of macromolecules that are difficult to be completed by many microporous zeolite molecular sieves, especially in catalytic reactions [1].

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There are many methods to synthesize mesoporous materials, such as sol-gel method, microwave assisted technique, chemical etching technique and template method.One of the most common and widely used methods is the template method.

At present, scientists have been able to add auxiliary organic molecules (such as co-surfactant), adjust the concentration of cations in surfactant and solution, change the amount of acid, stirring speed, aging temperature and crystallization time, etc., to change the pore size and morphology of mesoporous materials and enhance the orderness of pore distribution.

Surfactant template method is formed by surfactant molecule self-assembly micelles as the template, as in the synthesis process of the matrix, and adding inorganic silicon source, the use of surfactant and inorganic species charge matching, gathered body package ordered structures formed by inorganic species, caused by the method of chemical oxidation or electrochemical polymerization monomer polymerization in the template, after the calcination etc. A way to remove organic surface active agent, forming orderly porous materials. The surfactant template method is mainly divided into soft template method and hard template method according to the different types of template agents. Due to the different principles of these two methods, the fields of synthetic materials used are also different.

Soft template method, used in some certain circumstances can form some special morphology of materials as a template, which is based on molecular or intramolecular interaction to maintain its soft template of specific structure, such as surfactant and amphiphilic block copolymer, the use of hydrogen bonds between the precursor composition and template agent acting force and electrostatic force, etc, through the synergy of self-assembled replicate surfactants reverse phase, and then by calcining or extraction methods to remove the template, the resulting mesoporous materials, the template agent Lord be adopted by the anionic, cationic and nonionic surfactant.

Such as Li Yu, etc. [2] Using methyl orange and poly (N-vinyl pyrrolidone) as soft templates and $FeCl_3$ as oxidants, the nanotubular and rod-shaped polypyrrole products were successfully prepared

Hard template method, is based on covalent bonds to maintain its specific structure of hard template, such as porous silicon, organic polymer membrane, polystyrene ball and so on, is the skeleton structure has fixed porous materials as template agent, in the process of preparation of precursor on the surface of the channel that template agent by in situ growth assembly, hydrolytic condensation in the channel into the target product, then by calcining or etching methods to remove the template agent, mesoporous materials.

As Larson, etc. [3] The silica gel plate is used as a template. Firstly, a silk aqueous solution is coated on the silica gel plate, and then the silica plate is immersed in an aqueous solution containing pyrrole monomer. Chemical oxidation method is adopted to successfully deposit a layer of PPy with tubular structure on the surface of the silica gel plate.

In terms of the ionic types of surfactants, they can be divided into anionic, cationic, amphoteric and non-ionic surfactants. Due to their different structures and types, their properties are different and they have different applications in the synthesis of mesoporous materials.

Five kinds of surfactants used in mesoporous materials were prepared by template method

2. Cationic Surfactant

2.1. Introduce

Cationic surfactant is one of the most commonly used template agents, which is mostly used in soft template method, mainly organic amine derivatives containing nitrogen, which has good surface activity in acid, but in alkaline medium is easy to precipitate and lose its surface activity. However, as the most important cationic surfactant variety, quaternary ammonium salt

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surfactant ([R1R2N+R3R4]X-, it is soluble in both acidic and alkaline solutions, and has many applications in the template method.

2.1.1. Cetyl Trimethyl Bromide (CTAB)

Cetyl trimethyl bromide (CTAB) is one of the most common quaternary ammonium salt cationic surfactants, which have been widely used in the synthesis of mesoporous materials since the early stage due to its good stability, heat resistance, light resistance, pressure resistance and strong acid and alkali resistance.

2.1.2. Use CTAB to Synthesize Hexagonal Mesoporous Materials with Large Pore Size

In 1992, researchers at Mobil Oil Company [4]Cetyl trimethylammonium ions (CTA+) were mixed into solution, then alumina and trimethylammonium silicate solutions were added by stirring.The mixture is aged, filtered, and finally calcined to obtain the product. In other words, by using micellar structure surfactant aggregate as template, McM-41 was prepared with very ordered hexagonal row, and its pore diameter was greater than 2nm.

The result of this study is not only that the mesoporous material well replicates the structure of hexagonal liquid crystal, which makes people realize that soft templates such as lysogenic liquid crystal can guide the synthesis of mesoporous materials, but more importantly, it opens up a new way for the preparation of new materials, that is, liquid crystal templates can be used to regulate the size, morphology and structure of nanometers.

2.1.3. Use CTAB and APS to Synthesize Conductive Nanomaterials

Zhen Liu, Xinyu Zhang, etc [5] The reaction template was prepared by using CTAB and APS as surfactants, and then the monomer was added into the template for self-assembly reaction to synthesize conductive PEDOT nanomaterials, conductive polypyrrole nanomaterials and conductive polyaniline nanomaterials. They also used scanning electron microscopy and electrochemical techniques on the surface of high-temperature superconductors The structures of these three conductive polymers were analyzed [6] , including SEM and FTIR tests, and the comparison of the storage discharge energy, the electrical conductivity was evaluated.

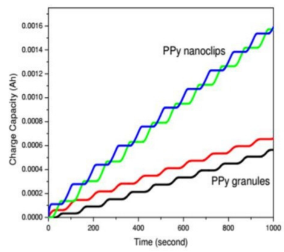

Figure S6. Charge/discharge capacity plot of PPy.Cl nanoclips and granules in the range of -0.5V~0.5V (vs. SCE) in aq. 1.0M NaCl electrolyte. Charge (green), discharge (blue) cycles for PPy nanoclips and charge (black), discharge (red) cycles for conventional (granular) PPy.Cl.

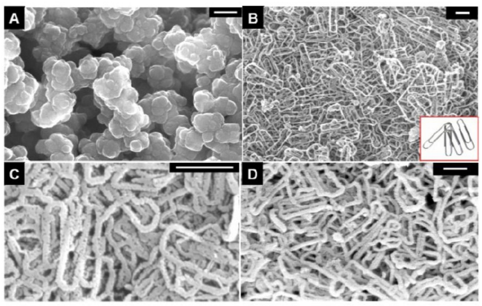

Figure S1. SEM images of (A) granular polypyrrole.Cl (scale bar: 200 nm); (B) polypyrrole.Cl nanoclips (scale bar 1 μm, Inset: digital picture of paper clips); (C) polyaniline.HCl nanoclips (scale bar: 1 μm); and (D) PEDOT.Cl nanoclips (scale bar: 1 μm).

Fig 1. Experiment picture

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In the above three experiments, CTAB and APS were used as surfactants to prepare the reaction template, and then monomers were added to the template for self-assembly. This conductive polymer is synthesized by the template method

Nanometer templates are similar to those prepared by traditional chemical oxidation or electrochemical methods in electrical conductivity, but the former is more effective than the latter in terms of discharge capacity

2.1.4. Use CTAB and APS to Synthesize PPY Nano-Materials with Various Structures

Yong Wang , Chunhong Yu[8]Hexadecyl trimethyl bromide (CTAB) crystal surface dislocation morphology was first discovered. By adding ammonium persulfate (APS) to the CTAB crystal suspension, the crystal morphology was changed from spiral to two-dimensional (2D) island. The helical and 2D island structures of these microcrystals can be used as templates for the synthesis of helical and cyclic polypyrrole (PPy) nanorires through direct chemical oxidation polymerization of pyrrole. Because these microcrystalline steps take precedence over oxidation reactions. The mechanism of adsorption of pyrrole oligomers on these crystalline steps was proposed for the growth of polypyrrole helical and circular nanowires.

3. Anionic Surfactant

3.1. Introduced

Production as surfactant in the development of the oldest and largest and most varieties of products, the anion surface active agent is a hydrophilic group to anionic surfactants, and according to its different hydrophilic group, anionic surfactant can be divided into carboxylates, sulfonates, sulfate salt and phosphate salt the four broad categories. However, because the silicate species is positively charged only under the condition of strong acidity ($pH < 2$), there are few synthesis methods using anionic surfactants to bond with it.

3.1.1. Application of Anionic Surfactant

3.1.2. Synthetic PPy with Different Conductivity

WenHuan etc.[9]Using p-toluene sulfonic acid (PTSA), sodium p-toluene sulfonic acid (TSA), dodecyl benzene sulfonic acid (DBSA), dodecyl benzene sulfonic acid (DBSA), methyl orange (Mo), sodium dodecyl diphenyl ether disulfonic acid (2 a1) as a soft template, such as a variety of anionic surface active agent to synthesis was prepared by the oxidation of iron trichloride under different morphology of polypyrrole (PPy) molecules, the grain size of inconsistencies also determines its conductivity differences, some of them such as the synthesis of Mo - PPy and TSA - PPy materials,It has high crystal orientation, high molecular chain ordering and few defects, so its electrical conductivity is also very superior, this kind of modified materials can be used in anti-static packaging and electromagnetic shielding fields.

3.1.3. Synthesis of Mesoporous Silica with Three-Dimensional Cage Cubic FD-3M Structure

Deng Shaoxin etc.[10]Mesoporous silica with 3d caged cubic FD-3M structure is successfully synthesized by using anion surfactant sodium laurocreatine (SAR-NA) as template and N-[3-(trimethoxysilicyl) propyl] ediamine (DAPS) or 3-[2-(2-amino-ethyl) ethyl amino] propyltrimethoxysilane (TAPS) as co-structure guiding agent. The transition of product structure from two-dimensional hexagonal structure with low interface curvature to three-dimensional caged-cubic FD-3M structure with high interface curvature was realized (with anion table)

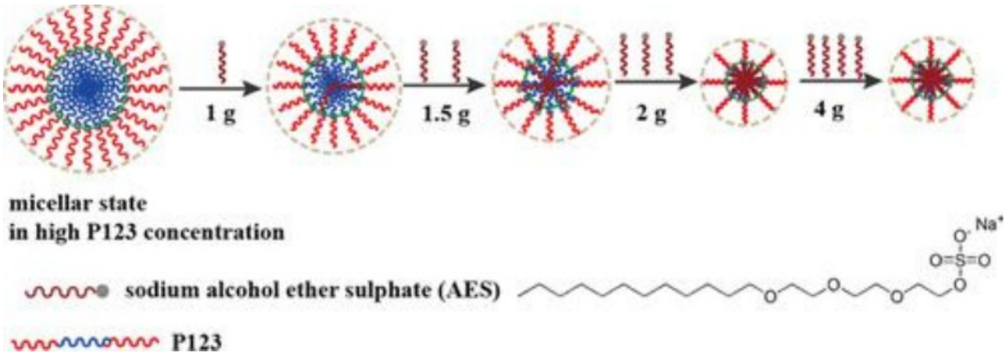

Fig 2. Synthesis and characterization of mesoporous silica with surfactant as template

3.1.4. Synthesis of Mesoporous Aluminosilicate Materials

In addition to mesoporous silica, mesoporous aluminosilicate is also a mesoporous material with excellent hydrothermal stability, so it can be used in many fields. For example, crystalline aluminosilicates with three-dimensional skeleton structure can be used to prepare boiling-stone, which can effectively prevent boiling phenomenon in the reaction process.

In the synthesis and application of mesoporous aluminosilicate (MAs), how to improve the utilization efficiency of P123 and reduce water consumption is a very important issue, which has attracted the common attention of scientists.

Xiaozheng Zhao, Xiaotong Mi, etc [11]MAs were synthesized at a high concentration of P123 (polypropylene oxide oxide - polypropane - polyethylene oxide triblock copolymer) using ethyl alcohol ether sulfate (AES) as a co-template. Their experiment reduced water consumption by about 77.3 percent compared to the traditional method, while the efficiency of P123 increased by 1.2 times. In the solution with high concentration of P123, micellar aggregation was formed in the absence of AES, which led to the decrease of the order degree of MAs. However, in the presence of AES, a well-dispersed micelle is formed, which facilitates the subsequent assembly process.

4. Non-ionic Surfactant

4.1. Introduced

As an important variety of production after anionic surfactant, nonionic surfactant, it is ether containing can generate hydrogen bonds with water base, free hydroxyl hydrophilic group to implement the dissolution of a substance, which determines its also has the stability of the high, not easily affected by acid and alkali, easy to dissolve in water and organic solvent, a series of characteristics, and this series of also determines the characteristics of it in the template method compared to other three kinds of the superiority of the surfactant.Nonionic surfactants are mainly divided into polyethylene glycol type and polyol type.

4.1.1. Application of Non-ionic Surfactant

4.1.2. Synthesis of Au Nanowires

Zhang Dongbai etc.[12]A nonionic surfactant ($C_{12}E_4$) formation of layered liquid crystals as templates, chloroauric acid ($HAuCl_4$) The water solution is the water phase and the reactant, and USES $C_{12}E_4$ Au nanowires were prepared by the reducibility of EO groups.

4.1.3. Synthesis of Novel Polypyrrole/Silica Nanocomposites

Midori Ikegame, Keisuke Tajima and others like Martin et al [13]Using a porous membrane filter to polymerize pyrrole, a polymer composite with a directed submicron scale tubular polypyrrole domain was obtained.[14] By using sol-gel method and using diacetylene surfactant as template, the copolymer was prepared in a well-arranged silicate nano-channel

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A novel polypyrrole/silicon dioxide nanocomposite was synthesized from mesostructure silicon dioxide composed of a yoked polymer, and the polypyrrole domain was formalized by a surfactant containing pyrrole, and the polypyrrole domain was isolated and insulated by a one-dimensional silicate nanochannel to ensure the common properties.

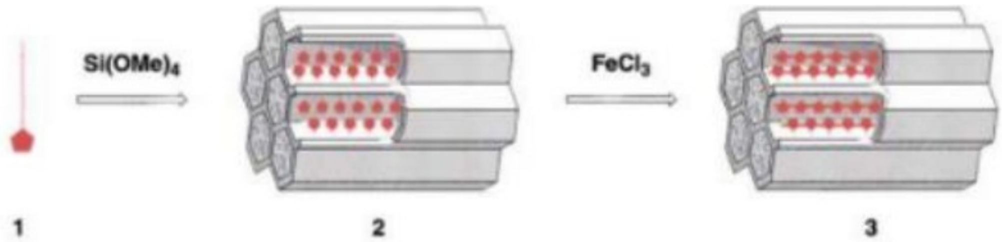

Figure 1. Schematic representation of the template synthesis of a polypyrrole/silica nanocomposite material (3) by oxidative polymerization of a pyrrole-containing surfactant (1) within a mesostructured silica (2).

Fig 3. The compactness of the silicate channel filled with yoke polymer

4.1.4. Synthesis of Mesoporous Silica Monomers with Various Structures

S. a. El -Safty *, etc[15] With Brij56 surfactant (C18EO10) as the structure guide agent, periodic mesoporous silica monomers with high degree of control over mesoporous morphology and surfactant phase structure can be successfully synthesized by direct template method. The synthesis process is mainly through direct template method using the three-dimensional (3-d) of mesoporous silica enhanced Brij56 phase topology structure, through adjusting Brij56 / TMOS quality than (about 35, 50, 70 and 75 wt %) of the phase behavior, respectively is the cubic spherical micelles, two-dimensional hexagonal, bicontinuous cubic and predictable mesophase of layered structure. In the process of removing Brij56 surfactant, the long-range ordered structure of silica remains unchanged, and the mesoporous molecular sieve obtained has the characteristics of large wall thickness, high surface area, uniform mesoporous channels, and clear morphology and structure.

5. Mixed Surfactant

5.1. Introduce

Generally speaking, mixed surfactants include anion-anionic, anion-amphoteric, anion-non-ionic and non-ionic surfactant compounding systems.

Additive synergies (synergistic effects) can be produced by the artificial synthesis of mixed surfactants through surfactant compounding. The resulting mixture has a better performance than the original single component, reaching the effect of "1+1>2", which can also be applied in the field of surfactant template method. When using the mixed surfactant as template, the molecular stacking parameters, molecular ordered aggregates and surface charge density of surfactants can be adjusted greatly. By changing the ratio of surfactants, the pore size and morphology of the mesoporous materials can also be changed.

5.1.1. Application of Mixed Surfactant

5.1.2. Anionic Surfactant/Cationic Surfactant

Jing-jing wang etc.[16]In the synthesis of mesoporous McM-48 molecular sieve mixtures using anion surfactant sodium dodecyl sulfate (SDS)/CTAB as template, due to the opposite charge between the parts

Neutralization reduces the charge density of micelles and makes the surface of the synthesized materials more hydrophobic. At the same time, the introduction of SDS as a common template agent effectively reduces the amount of CTAB, thus reducing the production cost.

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5.1.3. Anionic Surfactant/Cationic Surfactant

Generations, etc.[17] A hollow mesoporous SiO2 with uniform pore size, high specific surface area and pore volume and regular morphology was synthesized by the combination of N '-dodecyl -N, N-dimethyamidine bicarbonate and monthly sodium silicate in a certain proportion.

Huiming Lin, Guangshan Zhu, etc [18]Polymer-mesoporous silica nanoparticles were synthesized by double template technique.The cationic polymer quaternary ammonium poly[bis (2-chloroethyl) ether - Alt-1, 3-bis (3-(dimethylamine) propyl] urea](PEPU) and anionic surfactant sodium dodecyl sulfate (SDS) were used to form a homogeneous short chain system, and mesoporous silica spherical nanoparticles with diameter of 50-180 nm were induced.The mechanism of its formation was studied by transmission electron microscopy (TEM), and it was known that during the synthesis process, PEPU acted as a common template and generated a mesoporous structure to contain spherical nano-particles of silicon dioxide from PEPU.

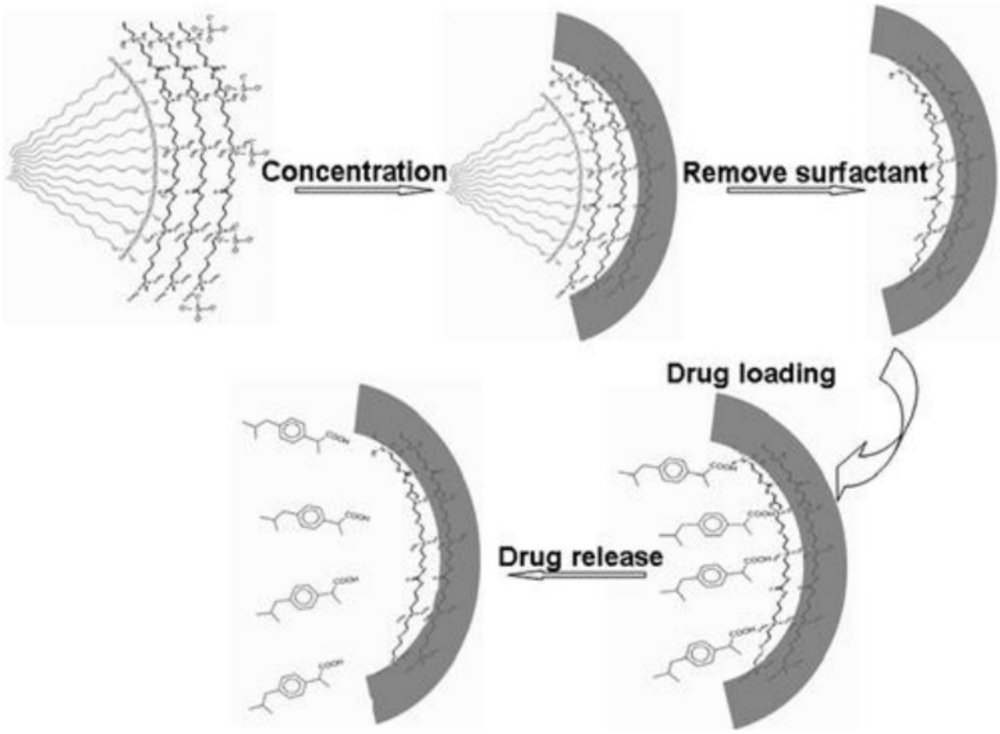

Fig 4. The synthesis process

6. Polyelectrolyte - Surfactant Mesocrystalline Complex

6.1. Introduction

Polyelectrolyte is a long chain polymer with ionizable groups. Polyelectrolyte is a kind of linear or branched synthetic and natural water-soluble polymer. Its structural unit contains ionizable groups. It can be used as thickener, flocculant, dispersant, emulsifier, suspension stabilizer and so on. Polyelectrolytes can be divided into polyacids and polybasic electricity according to their ionized groups in water

Solution quality. The polyacid electrolyte mainly includes polyacrylic acid and polymethyl methacrylate. And the polyalkali type electrolyte mainly includes polythene imine and polythene amine.

Polyelectrolyte - surfactant (PSMC) template method has become a common method for the preparation of multi-porous materials with different mesocrystalline phases and morphologies, including multi-porous silica and PMO[19], carbon[20]And titanium phosphate[21]. Multistage porous materials are an innovation on top of mesoporous materials[22-23] Compared with

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traditional single-layer porous materials, layered porous materials have more powerful load carrying capacity, which is of great significance for adsorption of macromolecules, as a catalyst carrier and as a hard template agent for porous functional materials[24-26].

Polyelectrolyte - surfactant template agents mainly include anionic polyelectrolyte/cationic surfactant complex, anionic polyelectrolyte/non-ionic surfactant complex and cationic polyelectrolyte/anionic surfactant complex.

6.1.1. Application of Polyelectrolyte - Surfactant Mesocrystalline Complex

6.1.2. Anionic Polyelectrolyte/Cationic Surfactant

The ionic self-assembly between anionic polyelectrolytes and cationic surfactants can form highly ordered mesocrystalline polyelectrolyte - surfactant complexes[27].

Chengxiang Shi, Huan Wang et al [28] Multistage porous monocrystalline silica colloids were synthesized using anionic polyelectrolyte/cationic surfactant as dynamic template.In the synthesis process, they used liquid crystal composite templates to guide negatively charged silicon precursors to obtain ordered mesostructures.At the same time, the electrostatic interaction between the polyelectrolyte chain and the surfactant micelles is disturbed or decomposed. Some polyelectrolyte chains are separated from the phase of the complex to form the chain domain, which serves as the template for the secondary nanopores in the calcined composite material.

However, due to the small size of cationic surfactant micelles, the pore size of mesoporous silica materials synthesized is generally lower than that of cationic surfactant micelles.

Near 2-3nm, for example, the M41S molecular sieves, synthesized in 1992 by researchers at Mobil Oil, have a pore diameter of more than 2nm, a successful breakthrough in mesoporous materials [29]. Therefore, the use of non-toxic, acid-base free, relatively low cost and high stability of non-ionic surfactants instead of cationic surfactants, anionic polyelectrolytes through the interaction between molecules formed by the ground complex is gradually attracted the attention of scientists.

6.1.3. Anionic Polyelectrolyte/Nonionic Surfactant

Chengxiang Shi, Huan Wang et al [28]Anion polyelectrolyte (PAA) and nonionic surfactant (P123) can also form a complex mesocrystalline structure through hydrogen bond interactions that can be used as a dynamic template for preparing grade porous silica.

Kit-6 (constructed in cubic Ia3-D) and SBA-15(constructed in two-dimensional hexagonal P6mm).These materials behave in an orderly manner.

The pore (about 7nm) and the embedded secondary nano-pore (about 15-50nm) with no perturbation of the long-range ordered mesoporous pore (about 15-50nm) have far exceeded the limit of the mesoporous material with a pore diameter of 2-3nm synthesized by the cationic surfactant. At the same time, the load performance of the mesoporous material is greatly improved due to the fact that its multistage pore diameter has no influence on its orderness.

6.1.4. Cationic Polyelectrolyte/Anionic Surfactant

As a basic polyelectrolyte, polyamine is also a very important strong cationic polyelectrolyte. It belongs to linear homopolymer, with abundant types and good water-solubility, and can be miscible with water at any ratio. Therefore, it can be mixed with anion surface active agent to form a complex to prepare mesoporous materials.

Shaoxin Deng, Chengxiang Shi[30]A novel biomimetic mesoporous silica preparation method was proposed. In other words, under the action of cationic polyamines, the anionic surfactant micelles were used as mesostructural templates, and the cationic polyamine chains were polymerized under the action of anionic surfactant micelles, so as to exert its ability to induce silica condensation[31] . Mesoporous silicon materials with good FD-3M symmetrical structure and three-dimensional hexagonal dense arrangement structure were prepared.

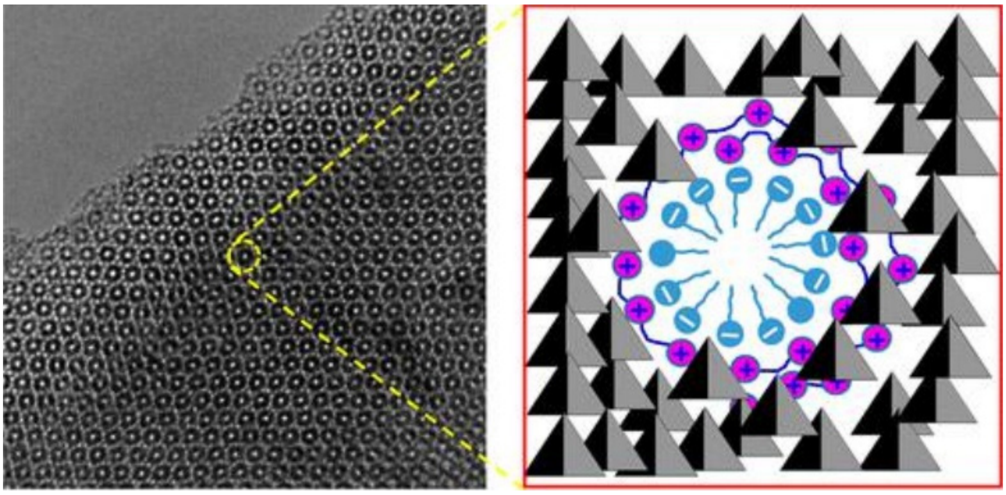

Fig 5. The final formed mesoporous silicon material map

7. Summary

This paper introduces the development of mesoporous silicate and mesoporous silica in recent ten years by using surfactants to prepare mesoporous materials by template method from the five aspects of cationic, anionic, non-ionic, mixed surfactant and polyelectrolyte - surfactant mesoporous complex[32-33].

Looking at the history of the mesoporous material template method, from the very beginning, researchers at Mobil Oil company [4]Using a cationic surfactant, hexadecyl trimethyl bromide (CTAB), as a surfactant, the ordered six-mesoporous material McM-41 was synthesized by template method, and the pore diameter of McM-41 was over 2nm, which achieved the breakthrough of the pore diameter limit of mesoporous material, Chengxiang Shi, Huan Wang et al[28]By anionic polyelectrolyte/nonionic surfactant, was synthesized and orderly in the hole and hole in the long range order without perturbation embedded subprime nanopores silica dielectric material, is not only by the cationic surfactants is far far breakthrough synthetic aperture in the limit of 2-3 nm mesoporous materials, but also because of its many level aperture is no effect on the order, and the load performance is much improved.

From the use of a single surfactant, to the application of mixed surfactant, and now through polyelectrolytes to modify the surfactant, enrich its own performance, to prepare better mesoporous materials, applied in a wider range of industries. Indeed, the progress of surfactants in formwork preparation of mesoporous materials has brought us too many surprises.

Believe in the near future, there will be more scientists to study the performance more good surfactant system to as templating agent, facilitates the preparation of mesoporous materials, and by changing the pore size of mesoporous materials, morphology and structure, to optimize the function of the mesoporous material itself more, can let mesoporous materials in the adsorption and separation, ACTS as a catalyst and carrier, and carrying big child substances such as enzymes, proteins, and drug controlled release and so on the application of the above are more diverse and functionalization.

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