Formation mechanism of anionic-surfactant-templated mesoporous silica (AMS)

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Abstract

This dissertation is focused on synthesis, characterization and formation mechanism of anionic-surfactant-templated mesoporous silica (AMS).

Structural control mechanisms of AMS are investigated. First, different ionization degree of anionic surfactant affected by the acidity or alkalinity of the synthesis system gives rise to different charging density of micelles and therefore determines the organic/inorganic interface curvature, producing mesophases from cage-type to cylindrical, bicontinuous and lamellar. Second, mesocage/mesocage electrostatic repulsive interaction affects the formation of cage-type mesostructure, which is derived from a full-scaled synthesis-field diagram of AMS. The mesocage/mesocage interaction changes with charge density of mesocages and gives rise to their different packing manners. Third, the structural properties of AMS materials could be tuned by molecular features of surfactant and co-structure-directing agent (CSDA), which could be utilized for the design of mesoporous silicas with special properties.

The pore size of AMS is found to be controlled by alkyl chain length, ionization degree of surfactant and the CSDA/surfactant ratio. Alkyl chain length of surfactant determines size of micelles and thus mesopores. Larger ionization degrees of anionic surfactant give rise to smaller pore sizes due to thermodynamic coiling of alkyl chains of surfactant. The hydrophobic interactions between the pendant organic groups of CSDA on the silica wall and the hydrophobic core of the micelles drive a contraction of the mesopores.

A mesoporous silica with novel bicontinuous cubic $Pn-3m$ structure has been prepared using a diprotic anionic surfactant. 3d-reconstruction of the structure shows that it has a bicontinuous structure composed of an enantiomeric pair of 3d mesoporous networks that are interwoven with each other, divided by a D surface. Inverse replication suggests the possible presence of ordered complimentary micropores in the material.
List of papers

This dissertation is based on the following papers.

I. Synthesis and characterization of mesoporous silica AMS-10 with bicontinuous cubic $Pn\text{-}3m$ symmetry  
C. Gao, Y. Sakamoto, K. Sakamoto, O. Terasaki, S. Che  

II. Formation mechanism of anionic surfactant-templated mesoporous silica  
C. Gao, H. Qiu, W. Zeng, Y. Sakamoto, O. Terasaki, K. Sakamoto, Q. Chen, S. Che  

III. Molecular design of the surfactant and the co-structure-directing agent (CSDA) toward rational synthesis of targeted anionic surfactant templated mesoporous silica  
C. Gao, Y. Sakamoto, O. Terasaki, K. Sakamoto, S. Che  

IV. Formation of diverse mesophases templated by diprotic anionic surfactant  
C. Gao, Y. Sakamoto, O. Terasaki, S. Che  

V. Molecular design of AEC tri-block anionic surfactant towards rational synthesis of targeted thick-walled mesoporous silica  
R. Gong, L. Han, C. Gao, M. Shu, S. Che  

VI. Formation of mesoporous $\text{Co}_3\text{O}_4$ replicas of different mesostructures with different pore sizes  
P. Shu, J. Ruan, C. Gao, H. Li, S. Che  
Other papers not included in this dissertation:

I. Mesostructured silica based delivery system for a drug with a peptide as a cell-penetrating vector
   C. Gao, I. Izquierdo-Barba, I. Nakase, S. Futaki, J. Ruan, K. Sakamoto, Y. Sakamoto, K. Kuroda, O. Terasaki, S. Che

II. Synthetic design towards targeted chiral anionic surfactant templated chiral mesoporous silica
    H. Jin, H. Qiu, C. Gao, S. Che
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1 Introduction

Highly ordered mesoporous materials have attracted broad interest in the societies of chemistry, physics and material science since the first discovery by the Kuroda group (Japan) and Mobil Company (US) in the early 1990s.[1,2] This kind of materials have large surface areas and pore volumes, tunable and uniquely distributed pore sizes within 2–50 nm, highly ordered mesostructures and variable surface properties, and therefore they are expected to find applications in fields of heterogeneous catalysis, separation, medicine, optics and electronics, etc.

Many kinds of mesoporous materials with diverse structures and pore sizes have been discovered to date by using different types of surfactants as the structure directing agent (“template”) and employing various synthesis strategies and methods. Cationic and nonionic surfactants are most commonly used as the template to form mesoporous materials. For example, M41S and SBA-15 were synthesized by using cetyltrimethylammonium bromide (CTAB) and Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) as the template, respectively. [2,3] However, for a long time, only lamellar or disordered mesoporous materials could be obtained by using anionic surfactants. Lately, Che et al firstly introduced co-structure-directing agents (CSDAs) into the synthesis of mesoporous materials, [4] and a family of highly ordered anionic-surfactant-templated mesoporous silicas (AMS) with highly ordered mesostructures have been prepared. [4–8]

Understanding the formation mechanism of mesoporous materials and how to control their structure are central topics, and researchers tried to find the solutions from different perspectives. Up to now, several theories on formation mechanism have been widely accepted, e.g. liquid crystal templating[2,9] and cooperative formation mechanism.[10,11] The packing of surfactants is considered to determine the mesostructure via surfactant packing parameter, $g$. [12–13] However, as the formation of mesoporous materials is a complicated process, it is impossible to disclose a mechanism that is perfect to be applied in most situations.

As AMS is a newly developed family of mesoporous materials, the formation mechanism of AMS mesostructures needs to be extensively explored for the purpose of future application, which is the main aim of this work. It has been demonstrated that this family of mesoporous materials have diverse structures, and therefore they are proper candidates for the study of structure formation mechanism of mesoporous materials.
1.1 The aim

The aim of this work has been to synthesize and characterize the AMS materials and to reveal the formation mechanism.

The first objective is to find the factors that affect the formation of AMS mesostructures. The investigations would demonstrate how much the final mesostructure of silica is dependent on these factors.

The second objective is to deduce reliable mechanisms from phenomenal observations, which are supposed to be widely applicable for the rational synthesis of mesoporous materials with novel properties.

The third objective is to try to find novel structures or structural properties, and solve them with the aid of techniques including powder X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption/desorption, electron crystallography, etc.
2 Background

This chapter is a review of the synthesis, mechanisms and applications of mesoporous materials. This dissertation is on the basis of these fundamental concepts.

2.1 Mesoporous materials: The definition

Porous materials are classified according to their pore size into microporous (< 2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm) materials.\[14,15\] Mesoporous materials were first discovered by the Kuroda group and Mobil Company in the early 1990s.\[1,2\] Since then this kind of materials have attracted wide interest of researchers because the pore size of these materials are beyond the limit of conventional zeolites, and thus can be used in a much more broad field, for example, heterogeneous catalysis with large molecules involved, biologic molecule manipulations, etc.

The characteristics of these materials include: (1) highly ordered mesostructures, (2) uniformly distributed pore size, (3) large surface area (~1000 m²/g) and pore volume (~1 cm³/g), (4) designable chemical composition and functionalizable surface and (5) controllable size and morphology.

Surfactant micelles or their liquid crystals are the “template” for the mesoporous materials. Many families of mesoporous materials have been developed so far, including M41S,\[2,9\] SBA,\[3,10,13,16–20\] HMS,\[21\] MSU,\[22\] KIT,\[23,24\] FDU,\[25–30\] HOM,\[31–37\] AMS,\[4–8\] etc. These materials were synthesized by using different surfactants, co-surfactants, synthesis conditions and methods.

2.2 Synthesis strategies of mesoporous materials

The synthesis of mesoporous material is on the basis of sol-gel chemistry.\[38\] In the synthesis system, the inorganic species (e.g. tetraethyl orthosilicate, TEOS) first hydrolyze and condense into an oligomeric silica sol, which is followed by a sol-gel transition due to the further condensation, accompanied by the self-assembly of surfactants and inorganic species to form mesostructures. Acid or base is the catalyst for the hydrolysis and con-
densation of silica precursors, and therefore commonly the reaction is conducted in either acidic or basic conditions.

The formation of mesoporous materials has been considered to be highly dependent on the interaction between organic (surfactants) and inorganic (silica oligomers) species. Different synthesis strategies are required for different types of surfactants to maintain these interactions.

Surfactants are classified into the following types according to their charging properties. (1) anionic (S⁻), with negatively charged headgroups, including alkyl carboxylate, phosphate, sulfate, sulphonate, etc. (2) cationic (S⁺), with positively charged headgroups, including alkyl quaternary ammonium salt, etc. (3) non-ionic (S⁰), with electrostatic neutral headgroups, including ethyloxide/propyloxide diblock or triblock copolymers, alkyl polyesters, alkyl amines, etc. Their interactions with inorganic species in the synthesis of mesoporous materials includes: S⁺I⁻, S⁺X⁻I⁺, S⁻X⁺I⁻, S⁰X⁺I⁻, S⁰I⁰, (S⁰H⁺)X⁻I⁺, etc.,[15,39] where S stands for surfactant, I stands for silica species and X represents inorganic salt. The charging of surfactant (S) is determined by its intrinsic property, while the charging of silica species is determined by pH of the synthesis system. Under acidic conditions (pH < 1.2) silica species are protonated and positively charged (I⁺), while under basic conditions (pH > 1.2) the silica species are negatively charged (I⁻), considering that the isoelectric point (pI) of silica is around 1.2. These interactions are visualized in Figure 1.

![Figure 1. Interactions between inorganic species and different kinds of surfactants in the formation of mesoporous materials.][15]

By using cationic and non-ionic surfactants as the template and employing S⁺I⁻, S⁺X⁻I⁺, S⁰X⁺I⁻, S⁰I⁰ and (S⁰H⁺)X⁻I⁺ synthesis strategies, various mesostructures have been achieved, including the families of M41S, [2,9] SBA[3,10,13,16–20] and FDU, [25–30] etc. However, strategies S⁻I⁺ and S⁻X⁺I⁻ using anionic surfactants as the template always gave rise to disordered mesophases or no mesostructure could be obtained. A possible reason is that under acidic condition anionic surfactant could be largely protonated, while under
basic conditions the interactions of counter-cations with surfactant and silicate ions are very weak.

To solve this problem, Che et al first introduced co-structure-directing agent (CSDA) into the anionic surfactant templating system, and a family of highly ordered mesoporous silicas AMS has been achieved. Figure 2 shows the schematic strategy of the synthesis of AMS materials. Amino silane, e.g. 3-aminopropyltrimethoxysilane (APS), or quaternary ammonium silane, e.g. N-(trimethoxysilyl)propyl)-N,N,N-trimethylammonium chloride (TMAPS), are two typical kinds of CSDA. The negatively charged headgroups of anionic surfactants interact electrostatically with the positively charged ammonium sites of the CSDAs, which acts as the driving force of the formation of highly ordered mesostructures. The alkoxy silane groups of the CSDA co-condense with tetraalkoxysilane and are subsequently assembled to form the silica framework. The trimethylene groups of the APS and TMAPS covalently tether the silicon atoms to the cationic ammonium groups. This novel route proves successful in producing a diversity of structures, including AMS-1~9 (Table 1).  

![Figure 2. The synthesis strategy of anionic-surfactant-templated mesoporous silica (AMS) using co-structure-directing agent.][4]

The synthesis method of mesoporous materials could be diverse. However, hydrothermal synthesis and evaporation induced self-assembly (EISA) are most commonly used. Hydrothermal synthesis is carried out in dilute aqueous systems at certain temperatures and pressures, and mesoporous silica solids crystallize and precipitate from the solution. Normally these materials have crystal-like morphology, highly ordered mesostructure and high hydrothermal stability. EISA is carried out in alcoholic solutions and meso-
porous material forms as the evaporation of alcohols proceeds. This method can afford mesoporous films and monoliths, which are of special interest in some applications.

Table 1. Synthesis conditions, structure and sorption properties of AMS-n.\cite{4-8}

<table>
<thead>
<tr>
<th>Mesophase</th>
<th>Surfactant, CSDA</th>
<th>Conditions</th>
<th>Mesostructure</th>
<th>Sorption properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Surface area (m²/g)</td>
<td>Pore volume (m³/g)</td>
</tr>
<tr>
<td>AMS-1</td>
<td>C₁₄GluA, TMAPS</td>
<td>Concentration of surf=1%, CSDA/Surf=2, Si/Surf=12</td>
<td>3d-hexagonal</td>
<td>501</td>
</tr>
<tr>
<td>AMS-2</td>
<td>C₁₂GluA, APS</td>
<td>Concentration of surf=1%, CSDA/Surf=2.5, Si/Surf=21</td>
<td>3d-cubic with modulations</td>
<td>963</td>
</tr>
<tr>
<td>AMS-3</td>
<td>C₁₀As, TMAPS</td>
<td>Concentration of surf=1%, CSDA/Surf=1, Si/Surf=10</td>
<td>2d-hexagonal p6mm</td>
<td>387</td>
</tr>
<tr>
<td>AMS-4</td>
<td>C₁₂AlaA, APS</td>
<td>Concentration of surf=1%, CSDA/Surf=0.75, Si/Surf=8.3</td>
<td>3d-cubic, hexagonal</td>
<td>760</td>
</tr>
<tr>
<td>AMS-5</td>
<td>C₁₂AlaA, APS</td>
<td>Concentration of surf=1%, CSDA/Surf=1, Si/Surf=4</td>
<td>lamellar</td>
<td>667</td>
</tr>
<tr>
<td>AMS-6</td>
<td>C₁₂AlaA, APS</td>
<td>Concentration of surf=0.7%, CSDA/Surf=0.75, Si/Surf=6.75</td>
<td>bicontinuous 3d-cubic P4 3/mnm</td>
<td>301</td>
</tr>
<tr>
<td>AMS-7</td>
<td>C₁₄GluSA, TMAPS</td>
<td>Concentration of surf=1%, CSDA/Surf=1.5, Si/Surf=16.5</td>
<td>3d-disordered</td>
<td>271</td>
</tr>
<tr>
<td>AMS-8</td>
<td>C₁₂GlyS, TMAPS</td>
<td>Concentration of surf=1%, CSDA/Surf=1, Si/Surf=10</td>
<td>3d-cubic P4 3/mnm</td>
<td>872</td>
</tr>
</tbody>
</table>

2.3 Formation mechanism of mesoporous materials

After the discovery of M41S and related solids, an increasing number of research teams focused on the understanding of their formation mechanisms. All models proposed so far are based on one principle: surfactant play a central role in directing the formation of the organic/inorganic mesostructure.

![Figure 3. A scheme for the synthesis mechanism of mesoporous silica proposed by scientists in Mobil Company.\cite{9}](image)

The mesostructure of M41S materials depends greatly on the surfactant concentration and hydrophobic chain length and on the presence of organic swelling agents dissolved in the hydrophobic spaces. This analogy with liquid crystal mesophases led scientists in Mobil Company to initially propose a mechanism that a templating process of a liquid crystalline phase was involved.\cite{2,9} The liquid crystal templating mechanism (Figure 3, route 1)
maintains that surfactant liquid crystal is the template for the mesoporous silica. The hydrolyzed silica source deposits and fills the hydrophilic domains of the liquid crystalline phase, and after solidification inorganic silica framework forms which copies the geometry of the liquid crystalline phase. This theory for the first time introduced the “template” concept which has been highly accepted as the central concept in the mechanism study of mesoporous materials.

However, the liquid crystal templating mechanism has been a matter of debate, as it has been realized that no preformed surfactant liquid crystalline phase exists in the synthesis precursor of mesoporous materials in the hydrothermal synthesis. The concentration of surfactant required for the formation of liquid crystal is very high, which could not be obtained in the dilute precursor solutions. Scientists in Mobil Company further proposed another route called cooperative formation mechanism, as shown in Figure 3 (route 2). This theory maintains that the surfactant liquid crystalline phase, which is the template of mesopores, is formed after the addition of silica source. The inorganic species direct the self-assembly process of the surfactant, forming hexagonal co-arrangements.

![Figure 4. A scheme for the cooperative formation mechanism proposed by Stucky et al.][11]

The cooperative formation mechanism of mesoporous silica was further advanced by Davis et al.[47,48] and Stucky et al.[10,11]. The Stucky’s theory has been widely accepted, which was inspired by the lamellar-to-hexagonal phase transformation.[49] Figure 4 presents the process of formation of
MCM-41 mesoporous silica from aqueous solution of CTAB and silica source. In an early stage, an ion-exchange occurs preferentially between silicate oligomers and CTAB in the precursor solution, and a CTA-silica complex is thus formed. The self-assembly of CTA-silica then happens to form a silicatropic liquid crystal (SLC) phase. A low-curvature lamellar phase is formed first because of the highly charged silica species and the charge density matching. When the condensation of silicate proceeds, the negative charge density of oligosilicate is dramatically reduced. This causes a rearrangement of surfactant and consequently a mesophase transformation to a high-curvature hexagonal one. The final phase is determined by the reaction coordinate when the solidification of the SLC is achieved.

The formation mechanisms, i.e. liquid crystal templating and cooperative formation, are valid when using different synthesis methods. It is known that the free energy of mesostructure formation ($\Delta G_{\text{meso}}$) is mainly composed of four terms, including the contributions of the organic-inorganic interactions ($\Delta G_{\text{inter}}$), the condensation of inorganic framework ($\Delta G_{\text{inorg}}$), the micellization of surfactant ($\Delta G_{\text{org}}$) and the free energy change of the solution ($\Delta G_{\text{sol}}$).[15,50]

In the process of hydrothermal mesostructure formation, $\Delta G_{\text{inter}}$ dominates the overall free energy change, and in this case cooperative formation mechanism is valid. The controlling factor of the mesophase determination is the organic/inorganic interaction.

The liquid crystal templating of mesoporous materials, e.g. the evaporation-induced self-assembly (EISA) synthesis of mesoporous films/monoliths [40–46] and the synthesis of HOM materials, [31–37] $\Delta G_{\text{org}}$ dominates the overall free energy reduction, i.e. the self-assembly of surfactant controls the formation of mesostructures. The liquid crystal phase is preformed before the addition of inorganic source.

2.3 Structural control of mesoporous materials

2.3.1 Structures of mesoporous materials

Mesostructure control has been an important research field since the discovery of mesoporous materials. Diverse mesophases have been disclosed to date, which can be divided into the following several types according to the geometry of their mesopores.

(1) Lamellar (L)

Alternative arrangement of organic layers and silica layers are present in this kind of materials. The removal of surfactant easily leads to a collapse of the mesostructure. A typical example is MCM-50.

(2) 2d-Hexagonal ($p6mm$)
The mesostructure has two-dimensional hexagonal arrangement of cylindrical mesopores. The plane group is \( p6mm \). Typical materials include MCM-41, SBA-15, SBA-3, AMS-3, etc.

(3) Bicontinuous cubic (\( Ia-3d, Pn-3m, Im-3m \))

These three types of bicontinuous cubic symmetry have been well discovered and recognized as liquid crystalline phases of soft-mater systems. In these structures the curvature of hydrophilic/hydrophobic interface is low and the mean curvature is zero. MCM-48 is the first mesoporous solids with bicontinuous structure.

In these mesoporous silica bicontinuous structures there is a tricontinuous mesopore/silica wall architecture, with two disconnected but interwoven mesopore networks divided by a silica wall grown along a gyroid (G), diamond (D) or primitive (P) minimal surface, for bicontinuous \( Ia-3d, Pn-3m, Im-3m \), respectively. Figure 5 shows the schematic structures of these mesophases.

Typical mesoporous materials having bicontinuous \( Ia-3d \) structure are MCM-48, KIT-6, FDU-5, AMS-6, etc. A typical mesoporous silica with bicontinuous cubic \( Pn-3m \) structure is AMS-10,\(^{53}\) which is discovered by this work and will be discussed in details in this paper. El-Safty \( et \) \( al. \) synthesized HOM-7 having \( Pn-3m \) symmetry,\(^{32}\) but no direct evidence was shown to prove the space group as well as the bicontinuous feature. Mesoporous material with bicontinuous cubic \( Im-3m \) structure was prepared by Wiesner \( et \) \( al. \), which was named “Plumber’s Nightmare”\(^{54,55}\)

![Figure 5. Scheme for bicontinuous cubic phases. A: G-surface and the \( Ia-3d \) network; B: D-surface and the \( Pn-3m \) network; C: P-surface and the \( Im-3m \) network.\(^{51,52}\)](image)

(4) Cage-type cubic (\( Pm-3n, Fm-3m, Im-3m, Fd-3m, etc \))

Cage-type mesophases are formed by packing of spherical micelles of surfactant in the synthesis. Therefore, the hydrophilic/hydrophobic interface curvature is high for these structures. Windows are present between cages to form 3d-connected network. \( Pm-3n, Fm-3m, Im-3m \) and \( Fd-3m \) are four
commonly seen cage-type cubic phases in mesoporous solids. The packing manners of cages in these structures are shown in Figure 6.

Typical $Pm-3n$ structured mesoporous silicas are SBA-1 and SBA-6. Two types of cages, as A and B shown in Figure 6A indicates, are present in the structure. Cage A is a six-membered ring, and cage B is a five-membered ring which is surrounded by twelve cages A. FDU-2 and AMS-8 are two typical $Fd-3m$ structured mesoporous silicas. In one unit cell of the structure, there are 16 small cages and 8 large cages. SBA-16 is the typical mesoporous silica for the structure $Im-3m$. The cages are the same size, each of which are connected by 8 surrounding cages. Cubic $Fm-3m$ is commonly intergrown with 3d-hexagonal structure, such as SBA-2 and SBA-12. Miya-saka et al synthesized and characterized a pure $Fm-3m$ mesophases by using C16-3-1 as the template in a dilute synthesis system, and they revealed that each cage are surrounded and connected by twelve adjacent cages.

Figure 6. The Scheme for the cage-type cubic mesostructures. A–D represents $Pm-3n$, $Fm-3m$, $Im-3m$, $Fd-3m$, respectively.\cite{6,56,57}

(5) Cage-type hexagonal ($P6_3/mmc$)
It often intergrows with $Fm-3m$ because of the similarity of these structures in the packing model (porosity, 74.05\%).\cite{58} The cage packing sequence of $P6_3/mmc$ is ABABAB..., while the packing of an $Fm-3m$ structure is in an order of ABCABC....

(6) Other mesophases ($P4_2/mnm$, $P4/mmm$, $c2mm$, $Pmmm$, etc).
$P4_2/mnm$ and $P4/mmm$ are two typical tetragonal mesophases. They are low-symmetry structures formed by packing of spherical micelles. A typical instance for $P4_2/mnm$ structure is AMS-9, synthesized by using C12GluA as the template and APS as the CSDA.\cite{8} $P4/mmm$ was synthesized by Zhao et
by using a four-headed rigid bola-form surfactant as the template. By using this method they also synthesized mesoporous silicas of \( Pmnm \) symmetry.\(^{[59]} \)

\( c2mm \) is a 2d-rectangular structure. SBA-8 has the structure of \( c2mm \), which was synthesized by using a rigid cationic surfactant R12 as the template.\(^{[60]} \)

2.3.2 Surfactant packing parameter, \( g \)

Researchers found that by investigating the surfactant packing parameter, \( g \), which was firstly proposed by Israelachvili \( et \ al.^{[12]} \) the resultant mesophases could be predicted to an extent.

\[ g = \frac{V}{a_0h}, \]

where \( V \) represents the volume of the hydrophobic tail, \( a_0 \) represents the effective headgroup area and \( h \) is the kinetic length of the hydrophobic tail of the surfactant.

The geometry of the mesopores is determined by parameter \( g \) as shown in Table 2. If \( g = 1/3 \), spherical micelles are formed, which give rise to cage-type mesophases. If \( g = 1/2 \), cylindrical micelles are formed, and in this case a 2d-hexagonal mesophases is favored. If \( g = 1 \), a layered structure is formed. If \( g \) value is between 1/2 and 2/3, bicontinuous cubic phases could be resulted, having a hydrophilic/hydrophobic interface curvature in between lamellar and 2d-hexagonal mesophase.\(^{[13]} \)

Table 2. The mesophases resulted from different \( g \) values of surfactant.\(^{[13]} \)

<table>
<thead>
<tr>
<th>( g )</th>
<th>Mesophases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3</td>
<td>Micellar Cubic (( Pm-3n, Im-3m, Fd-3m ), etc), 3d-hexagonal (( P6_3/mmc )), Tetragonal (( P4_2/mnm, P4/mm )), etc</td>
</tr>
<tr>
<td>1/2</td>
<td>2d-hexagonal (( p6mm ))</td>
</tr>
<tr>
<td>1/2-2/3</td>
<td>Bicontinuous cubic (( Ia-3d, Im-3m, Pn-3m ))</td>
</tr>
<tr>
<td>1</td>
<td>Lamellar</td>
</tr>
</tbody>
</table>
2.3.3 Structural control of mesoporous silicas

In the synthesis of mesoporous materials, the energetics of self-organization has been thought of in two parts. One part is the packing energetics of the surfactant,\(^{[10]}\) and the other depends on charge density matching between the surfactant and the inorganic species.\(^{[49]}\) The surfactant packing depends on the molecular geometry of the surfactants, such as the number of carbon atoms in the hydrophobic chain,\(^{[61]}\) the degree of chain saturation,\(^{[12]}\) the size or charge of the polar headgroup,\(^{[10,62]}\) and the molecular shape.\(^{[59]}\) In addition, it has been reported that the packing of the surfactant is also affected by the solution conditions, including the surfactant concentration,\(^{[63]}\) the presence of co-surfactant\(^{[61,64]}\) and counterion,\(^{[65–67]}\) and temperature.\(^{[68]}\)

(1) Geometry of surfactant

![Figure 8. Suggested mesostructures as a function of the hydrophilic-hydrophobic balance in amphiphilic block copolymer blends.\(^{[62]}\)](image)

The structure of mesoporous materials is highly dependent on the geometry of surfactant, including the size and charging of headgroups, length and saturation of hydrophobic tail and its molecular shape. For an instance, Huo \textit{et al} disclosed that cetyltrimethylammonium bromide (CTMAB) leads to formation of 2d-hexagonal \((g = 1/2)\) structure easily, while cetyltriethylammonium bromide (CTEAB) having a larger headgroup gives preferably 3d-cubic \(Pm-3n\) \((g = 1/3)\).\(^{[13,16]}\) Kim \textit{et al} found that when using nonionic surfactant as the template to synthesize mesoporous silicas, the mesostructure changes in series of lamellar, 2d-hexagonal \(p6mm\), 3d-hexagonal \(P63/mmc\), and cubic \(m-3m\).\(^{[62]}\) Zhao \textit{et al} used four-headed rigid bola-form surfactant to form mesostructures of low-symmetry, \textit{e.g.} \(P4/mmm\) and \(Pmnm\).\(^{[59]}\) Therefore, the molecular design is an effective route to design the properties of mesostructures, which would be discussed in details in this paper for the AMS systems.

(2) Co-surfactant

The addition of co-surfactant into the synthesis system of mesoporous materials is an effective way to control the mesostructure. For an instance, 1,3,5-trimethylbenzene (TMB) tends to aggregate at the tail region of surfactant, which lowers the hydrophilic/hydrophobic interface curvature.\(^{[13]}\) If
polar substances e.g. alkyl alcohols are added in the synthesis, they easily get to the hydrophilic/hydrophobic interface which enlarges the hydrophobic volume, and a low curvature mesostructure could be obtained, e.g. KIT-6.[13,24,64]

(3) Concentration of surfactant
An increase in the concentration of surfactant leads to a transformation of spherical micelles into cylindrical and lamellar in surfactant solutions, which is reflected in formation of mesostructures. For example, when increasing the concentration of CTAB in the synthesis of MCM-41, MCM-48 with bicontinuous cubic Ia-3d and lamellar structures would be obtained in succession.[63]

(4) Counterions
The use of counterions in the synthesis of mesoporous materials would alter the state of the micelles. Che et al synthesized different mesostructures by using Br\(^-\), Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\) as the counterions of the CTEA\(^+\), and they propose that the size of the ions are the key factors of the phase transformation.[65] Wang et al found that in the nonionic-surfactant-templating systems the type of the salt could change the mesostructure of silica materials, due to the salting-in and salting-out effects of the counterions.[67]

(5) Charging density matching
Monnier and Tolbet et al found that a phase transformation of lamellar to hexagonal occurs during the formation of MCM-41. The charging density matching between surfactant and charge-decreasing silica wall was thought to dominate the process.[49]

2.4 Nanocasting: a hard templating method
Nanocasting is a synthesis method using inorganic solids as the template.[69–71] Therefore, it is also referred to as hard templating. Nanocasting is a versatile route to synthesize mesoporous materials with different chemical compositions and structures.

Nanocasting was firstly introduced to the synthesis of mesoporous materials by Ryoo and co-workers to synthesize mesoporous carbon,[72–75] and several mesoporous metals,[76,77] metal sulfides,[78] nitride[79] and oxides[80–90] have been fabricated by using this method. The advantages of nanocasting include: (1) The template materials could be diverse in structure and dimension, (2) The chemical composition and structure could be well designed.

The process of nanocasting involves infiltration of precursors of guest materials into mesoporous host and subsequent removal of the host materials. Therefore, an inverse replication of host structure and morphology could be achieved. However, structural deformation occurs in some cases. Ryoo and co-workers found that when preparing replica of MCM-48 only one set of
the bicontinuous mesochannels was replicated and therefore a phase transformation from \(Ia-3d\) to \(I4_132\) was observed (Figure 9).\[^{72}\]

The inverse replication provides a feasible method to probe the properties of host mesoporous materials. For an instance, Sakamoto \textit{et al} proposed the existence of the ordered complementary micropores in the thinnest parts of the silica walls of large-pore \(Ia-3d\) silica by investigating structures of the carbon replica.\[^{91}\] Shin \textit{et al} investigated the micropore connectivity of mesopores in SBA-15 by carbon inverse replication.\[^{92}\]

\[\text{Figure 9. Structural deformation of } Ia-3d \text{ structure in nanocasting.}\]

\[\text{Mesoporous Silica} \quad \text{Metal oxide/Silica} \quad \text{Metal oxide}\]

2.5 Applications of mesoporous materials

Strictly speaking, there is not yet a breakthrough in industrial applications of mesoporous materials.\[^{93,94}\] However, it has been a growing interest of research in the recent years, and the focus is in the fields of chemical industry, bio-application and functional materials, \textit{etc}. This section presents a brief overview on the current application research of mesoporous materials.

2.5.1 Chemical industry

\textit{Catalysis} Mesoporous materials have large surface area, defined pore structure and large pore size. For reactions with large molecules involved, mesoporous materials based catalysts show better performance than traditional zeolitic catalysts.\[^{95,96}\] Therefore, it opens new possibilities for many heterogeneous catalysis reactions. Kozhevnikov \textit{et al} showed when loading the heteropoly acid (HPA) into mesoporous materials, the catalysis reactivity of the materials was significantly enhanced which became close to that of concentrated sulfuric acid.\[^{97}\]

\textit{Confined reactor} Mesoporous materials provides cavities of 2–50 nm dimensions which are highly uniform, therefore they can be used as confined reactors, for many reactions \textit{e.g.} polymerization.\[^{98,99}\] The lifetime of free radicals is elongated and the distribution of molecular weight becomes narrower by using this nano-reactor.
2.5.2 Bio-application

Bioadsorption and biocatalysis The encapsulation of enzymes and other proteins into mesoporous materials has attracted considerable attention over the past few years. Biocatalysts and bio-sensors have been developed based on the absorbed proteins in the mesopores.\textsuperscript{[100]}

Carrier for biomedicines Mesoporous material was first used as a drug carrier by Vallet-Regi et al.\textsuperscript{[101]} They further demonstrated that the properties of mesoporous materials, \textit{e.g.} pore size, surface area, pore volume, functionalities, affect dramatically the release kinetics of drugs.\textsuperscript{[102–105]} Based on the mesoporous materials, researchers also developed various kinds of “smart” devices, which can release the drug in response to external stimuli, such as pH\textsuperscript{[106–110]} temperature,\textsuperscript{[111,112]} light irradiation\textsuperscript{[113–116]} and redox reagents,\textsuperscript{[117–119]} etc, which have potential applications in targeted and controlled drug delivery systems.

2.5.3 Functional materials

Energy storage The high surface area and large pore volume of mesoporous material makes it possible for energy storage devices, \textit{e.g.} hydrogen storage.

Low-k material Mesoporous materials have large porosities, and therefore they have low dielectric constant ($k$), which may find use in electronic industries \textit{e.g.} integrated circuit.\textsuperscript{[120,121]}
3 Experimental

3.1 Chemicals

The chemicals listed below were purchased and used without further purification.

*Inorganic compounds* 3-Aminopropyltrimethoxysilane (APS, TCI), methyldimethylaminoethyltrimethoxysilane (MAPS, Chisso), dimethyldimethylaminoethyltrimethoxysilane (DMAPS, Gelest), \(N\)-((trimethoxysilylpropyl)-\(N\),\(N\),\(N\)-trimethylammonium chloride (TMAPS, Azmax), tetraethyl orthosilicate (TEOS, TCI), \(\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\).

*Commercial Surfactants* Lauric acid (C\(_{12}\)AA, TCI), lauric acid sodium salt (C\(_{12}\)AS, TCI), myristic acid sodium salt (C\(_{14}\)AS, TCI), palmitic acid sodium salt (C\(_{16}\)AS, TCI), stearic acid sodium salt (C\(_{18}\)AS, TCI), \(\text{C}_{12}\text{H}_{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_{10}\text{CH}_2\text{COONa (AEC, Kao Chemicals, C}_{12}\text{H}_{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_{10}\text{H (Brij-22, Sigma)}.

3.2 Synthesis of anionic surfactants

Anionic surfactants derived from amino acids (glutamic acid, alanine, valine, etc) were synthesized, and a typical process is described as follows.

In a typical synthesis of \(N\)-myristoyl-L-glutamic acid (C\(_{14}\)GluA), 49.3 g (0.2 mol) of myristoyl chloride and 8.0 g (0.2 mol) of sodium hydroxide in 20 ml of water were added to a solution prepared from 35.5 g (0.24 mol) of L-glutamic acid in 140 ml of water and 120 ml of acetone and 19.2 g of sodium hydroxide with stirring at 30 °C and \(\text{pH} 12\) over a period of 20 min. The reaction mixture was stirred for one additional hour, cooled, and acidified to \(\text{pH} 1\) with sulfuric acid. The precipitated solid C\(_{14}\)GluA was washed in petroleum ether to obtain the pure crystals.

Such surfactants include: \(N\)-lauroyl-L-glutamic acid (C\(_{12}\)GluA), \(N\)-myristoyl-L-glutamic acid (C\(_{14}\)GluA), \(N\)-stearoyl-L-glutamic acid (C\(_{18}\)GluA), \(N\)-lauroyl-L-alanine (C\(_{12}\)AlaA), \(N\)-myristoyl-L-glycine (C\(_{14}\)GlyA).

The sodium salts of the above surfactants were obtained by neutralization with \(\text{NaOH, e.g., C}_{14}\text{GlyS and C}_{14}\text{GluAS were obtained by neutralization of their acid form surfactant with equivalent amount of NaOH. As C}_{14}\text{GluA is a
diprotic surfactant, the sodium salt of it obtained by neutralization with 2 equivalent amount of NaOH was denoted as C₁₄GluS.

3.3 Synthesis of anionic-surfactant-templated mesoporous silica (AMS)

Typical synthesis procedures of anionic-surfactant templated mesoporous silicas are described as below.

Example 1: (TMAPS as the CSDA)

In a typical synthesis of AMS-10, 0.357 g C₁₄GluA (1 mmol) was dispersed in 35 g deionized water at 80 °C and then 0.75 g 1 M NaOH was added with stirring. After the surfactant solution was cooled to 60 °C, a mixture of 3.12 g TEOS (1.5 mmol) and 0.773 g TMAPS (50 wt% in methanol, 1.5 mmol) was added with stirring. After 10 minutes, the stirring was stopped and the reaction mixture was aged at 60 °C for 2 days. The precipitate was filtered, dried and then calcined at 550 °C for 6 hours or extracted to give surfactant-free mesoporous silica.

Example 2: (APS as the CSDA)

In a typical synthesis, 0.413 g C₁₈GluA (1 mmol) was dispersed in 41 g deionized water and stirred to obtain a milky solution. A mixture of 3.12 g TEOS (1.5 mmol) and 0.358 g APS (2 mmol) was added in the same time with stirring. After 10 minutes, the stirring was stopped and the reaction mixture was aged at 80 °C for 2 days. The precipitate was filtered, dried and then calcined at 550 °C for 6 hours or extracted to give surfactant-free mesoporous silica.

Example 3: (AEC surfactant as the template)

In a typical synthesis, a mixture of 0.109 g TMAPS (50 w% in methanol, 0.212 mmol) and 1.18 g TEOS (5.67 mmol) was added to a mixture of 0.909 g (22 w% in water, 0.283 mmol) C₁₂H₂₅O(CH₂CH₂O)₁₀CH₂COONa (AEC), 20 g deionized water and 0.07 g 1 M HCl at 60 °C with stirring. The initial pH before addition of TMAPS and TEOS was measured to be 6.2. After 10 min, stirring was stopped and the reaction mixture was aged at 80 °C for 2 days. The precipitate was filtered, dried and calcined at 550 °C for 6 h or extracted to give template-free mesoporous silica.

3.4 Removal of surfactant from AMS by extraction

Extraction method of AMS is dependent on the type of CSDA used in the synthesis. The procedures here are described in our previous paper.¹²²

Extraction of AMS prepared with TMAPS as the CSDA
Typically, 0.5 g AMS was dispersed in 100 ml of ethanolic solution containing 90 ml ethanol and 10 ml HCl (35 wt%) and the mixture was refluxed at its boiling temperature for 12 h. The solids were recovered by filtration, washed with ethanol and dried at 80 °C overnight.

**Extraction of AMS prepared with APS as the CSDA**

Typically, 0.5 g AMS was dispersed in 100 ml ethanol containing 20 ml NH₂C₂H₄OH, or in 100 ml ethanol containing 4 g CH₃COONH₄ and 20 ml H₂O. The mixture was refluxed at its boiling temperature for 12 h. The solids were recovered by filtration, washed with ethanol, dried, and the above extraction procedure was repeated.

### 3.5 Synthesis-field diagram of AMS

Preparation of synthesis-field diagram of AMS could lead to further understandings of mesophase formation conditions and their formation mechanism.

**Table 3. Mol fractions of C₁₄GluA/NaOH/TMAPS to achieve the synthesis-field diagram of AMS.**

<table>
<thead>
<tr>
<th>Label</th>
<th>C₁₄GluA</th>
<th>NaOH</th>
<th>TMAPS</th>
<th>Label</th>
<th>C₁₄GluA</th>
<th>NaOH</th>
<th>TMAPS</th>
</tr>
</thead>
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<td>A1</td>
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<td>0.333</td>
<td>0.433</td>
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<tr>
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<td>0.267</td>
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<td>0.233</td>
<td>0.433</td>
</tr>
<tr>
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<td>0.200</td>
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<td>I6</td>
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<td>0.600</td>
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</tr>
<tr>
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<td>0.500</td>
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<td>C2</td>
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<tr>
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<td>0.267</td>
<td>0.367</td>
</tr>
<tr>
<td>D1</td>
<td>0.100</td>
<td>0.500</td>
<td>0.400</td>
<td>J6</td>
<td>0.433</td>
<td>0.233</td>
<td>0.333</td>
</tr>
<tr>
<td>D2</td>
<td>0.200</td>
<td>0.400</td>
<td>0.400</td>
<td>K1</td>
<td>0.333</td>
<td>0.433</td>
<td>0.233</td>
</tr>
<tr>
<td>D3</td>
<td>0.500</td>
<td>0.300</td>
<td>0.400</td>
<td>K2</td>
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<td>0.367</td>
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<tr>
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<tr>
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</tr>
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<td>0.350</td>
<td>0.400</td>
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<tr>
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<td>0.600</td>
<td>0.200</td>
<td>N4</td>
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<td>0.317</td>
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</tr>
<tr>
<td>F2</td>
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<td>0.500</td>
<td>0.200</td>
<td>O1</td>
<td>0.250</td>
<td>0.400</td>
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</tr>
<tr>
<td>F4</td>
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<td>0.300</td>
<td>0.200</td>
<td>P1</td>
<td>0.267</td>
<td>0.417</td>
<td>0.317</td>
</tr>
<tr>
<td>G1</td>
<td>0.133</td>
<td>0.233</td>
<td>0.633</td>
<td>P2</td>
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<td>0.384</td>
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</tr>
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<td>G2</td>
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<td>0.167</td>
<td>0.667</td>
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</tr>
<tr>
<td>G3</td>
<td>0.233</td>
<td>0.133</td>
<td>0.633</td>
<td>P4</td>
<td>0.317</td>
<td>0.317</td>
<td>0.367</td>
</tr>
<tr>
<td>H1</td>
<td>0.133</td>
<td>0.333</td>
<td>0.533</td>
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<td>H4</td>
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<td>0.567</td>
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<td>W</td>
<td>0.267</td>
<td>0.333</td>
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</tr>
</tbody>
</table>

We chose diprotic C₁₄GluA as the referenced structure-directing agent (SDA), because it has two carboxylate groups, which creates the possibility of forming different mesophases with highly curved organic/inorganic interface curvatures as well as mesophases with reduced curvature. Water soluble
TMAPS, having a permanent positive charge, was chosen as the CSDA, which interacts with anionic surfactant in an electrostatic way and serves as the counterion of the anionic surfactant. The amount of TEOS in the synthesis of AMS within a certain range does not have significant effects on the curvature of the resultant mesophase. Therefore, the key factors of the mesophase formation have been determined as C_{14}GluA, TMAPS and NaOH, the compositions of which have been changed to get the full picture of the diagram. Sixty-four compositions were carefully chosen to complete the synthesis-field diagram as shown in Table 3.

When preparing the C_{14}GluA/NaOH/TMAPS tri-component synthesis-field diagram, the following conditions were kept constant: concentration of the surfactant in water = 1 wt%; TEOS/surfactant = 15; synthesis temperature: 70 °C.

### 3.6 Co_{3}O_{4} replication of AMS-10

Nanocasting replication has the potential possibility to reveal the properties of mesoporous materials and to create novel materials with unique composition and structures.

A typical procedure of the synthesis of Co_{3}O_{4} material by using AMS-10 (bicontinuous cubic Pn-3m) as the hard template is as follows. The AMS-10 was first calcined at 550 °C for 6 h to give the mesopores. 0.75 g Co(NO_{3})_{2}·6H_{2}O (98% Aldrich) was dissolved in 16 ml ethanol followed by addition of 0.5 g AMS-10 mesoporous silica templates. The mixture was stirred at room temperature until nearly dry powder had been obtained. The sample was then heated slowly to 300 °C and calcined at the same temperature for 3 h to pyrolyze the nitrate. The impregnation procedure was repeated twice with 0.4 g Co(NO_{3})_{2}·6H_{2}O and 0.25 g Co(NO_{3})_{2}·6H_{2}O dissolved in 16 ml ethanol, followed by calcination at 550 °C for 5 h with a ramp of 1 °C/min for metal oxide to crystallize. The resulting samples were treated with 10% HF to remove the silica template, centrifuged, washed with water and ethanol, and then dried at 60 °C in air.

### 3.7 Characterizations

The common characterization techniques of mesoporous materials include powder X-ray diffractions (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and nitrogen adsorption/desorption, etc.
3.7.1 Structure determination

The structure of mesoporous materials could be well characterized by combination of XRD and TEM techniques.

In XRD characterization, X-ray detects the electron density variation in the mesoporous crystals, which further gives diffraction patterns at specific Bragg angles determined by the periodicity of the mesoporous crystal. Therefore, XRD pattern allows determination of unit cell parameters and space group. However, normally only a few peaks could be observed in the recorded patterns, because of which TEM observation is essential to aid the structural resolution. In a TEM characterization, electrons are used to detect the electrostatic potential variation of the mesoporous crystal, which gives more detailed structural information, and the determination of symmetry is more facile and convinced.

Moreover, structure of mesoporous materials could be well resolved by electron crystallography (EC) reconstruction, which offers the electrostatic potential distribution and mesopore connectivity. It is on the basis of electron microscopy as well as nitrogen adsorption. [56]

In this work, powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC using Cu Kα radiation (40 kV, 20 mA) at the rate of 1.0 ° 2θ /min over the range of 1–6 ° 2θ. High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL JEM-3010 microscope operating at 300 kV (Cs = 0.6 mm, resolution 1.7 Å). Images were recorded with a CCD camera (MultiScan model 794, Gatan, 1024×1024 pixels, pixel size: 24×24μm) at 50K –80K magnification under low-dose conditions. The structure of AMS-10 was resolved by EC reconstruction.

3.7.2 Morphology observation

The microscopic morphological features were observed by using SEM. In the SEM characterization, a scanning electron beam is used to probe the surface information of the sample. Normally secondary electrons are collected to get the morphological information.

In this work, morphologies of mesoporous materials were observed by using a SEM (JEOLJSM-7401F). An accelerating voltage, 1 kV (resolution: 1.4 nm) was chosen for all mesoporous silica samples.

3.7.3 Porosity characterization

The surface area, pore size and pore volume of mesoporous materials can be detected by nitrogen adsorption and desorption. It is carried out at the temperature of liquid nitrogen (-196°C), and nitrogen molecules are allowed to adsorb on the surface of materials. The capillary condensation pressures
are different for materials with different pore size, which makes it possible for determination of porous properties. Mesoporous materials show type IV isotherms, and three well-distinguished regions of the adsorption isotherm are present including monolayer-multilayer adsorption, capillary condensation and multilayer adsorption on the outer surface.

In this work, nitrogen adsorption/desorption isotherms were measured at -196°C on a Quantachrome Nova 4200e volumetric adsorption analyzer. Before the adsorption measurements, all samples were degassed at 200 °C in the port of the adsorption analyzer for 4 hours. Specific surface areas were calculated via the Brunauer-Emmett-Teller (BET) model in regions applicable to the derivation of the model between \( P/P_0 \) values of 0.05–0.3. The total pore volume was determined from the uptake of nitrogen at a relative pressure of \( P/P_0 \approx 0.99 \). Pore size distribution curves were obtained by using the Barrett-Joyner-Halenda (BJH) method. The calculation was based on the adsorption branch of the isotherms, if no additional notes were made. The pore sizes of the cubic mesoporous silicas are for comparison only, as the method is on the basis of cylindrical pore geometry, and the pore size is usually underestimated because of the approximation of the BJH method.\(^{[123]}\)

The wall-thickness \( (w) \) of mesoporous silicas was calculated combining the unit-cell parameter \( (a) \) derived from XRD pattern and pore diameter \( (d) \) derived from nitrogen adsorption/desorption. For bicontinuous cubic \( Pn-3m \) symmetry, \( w \) was determined as \( d_{110} - d \), i.e. \( w = a/1.4142-d \). (Structure model, reference 53). For 2d-hexagonal \( p6mm \) symmetry, \( w \) was calculated as \( a-d \).
4 Results and Discussion

In this chapter, formation mechanisms of anionic-surfactant-templated mesoporous silicas (AMSs) are discussed, including the following parts: (1) Ionization degree dominated structure formation; (2) Mesocage interactions controlled cage-type mesophase determination; (3) Molecular design towards specific structural properties. Besides, pore size control of AMS and the synthesis and characterization of a new bicontinuous AMS phase, \( Pn-3m \), are described in details.

4.1 Structural control by ionization degree of anionic surfactants

4.1.1 Mechanism of structural control by ionization degree of surfactants

Anionic surfactants are used in great volume because of their highly potent detergency and low cost of manufacture. Many kinds of anionic surfactants are commonly used, including alkyl sulfonate, sulfate, phosphate and carboxylate, etc. Among these, carboxylate (or carboxylic) surfactants are of special interest because of the diversity in the types and wide use in fine chemistry industry.

Carboxylic surfactants, including fatty acids and amino acid surfactants, etc., are common anionic surfactants. Unlike the quaternary ammonium cationic surfactants, carboxylic acid surfactants are weak acids, with a \( pK_a \) of about 1–5. Therefore, the equilibrium can be usually reached between the electrostatic neutral and the negatively charged surfactant molecules in solution:

\[
\text{Alkyl carboxylic acid (neutral)} \rightleftharpoons \text{Alkyl carboxylate (negative)} + \text{H}^+ 
\]

The degree of ionization of the surfactant (molar ratio of charged/total surfactant) can readily be changed in the presence of additional acid or base, which causes differences in the charge density of the micelles and results in different surfactant arrangements.
Figure 10. The charge density on the micelles, determined by the degree of ionization of the anionic surfactant, can vary, and results in different hydrophilic/hydrophobic interface curvatures. a, smaller interface curvature created by lower degree of ionization; b, larger interface curvature created by larger degree of ionization.

As shown in Figure 10, when the alkalinity of the synthesis system is low, the ionization equilibrium of anionic surfactant favors the formation of neutral charged species, which makes a low charge density of the micelles and therefore low electrostatic repulsions between surfactant headgroups. As a result, the effective surfactant headgroup area is small, which gives a large surfactant packing parameter, $g$, according to its definition $g = V/a_0 h$. As a consequence, the resultant silica mesoporous structure has a low hydrophilic/hydrophobic or organic/inorganic interface curvature. When the alkalinity of the synthesis system of AMS rises, on the other hand, anionic surfactants become more ionized, which leads to an increase in the repulsive electrostatic forces between headgroups of surfactants and thus high organic/inorganic interface curvature of the resultant mesophase.

It is worth noting that in the discussion of electrostatic interactions between charged headgroups of surfactant (also charged mesocages in Section 4.3), the dielectric constant ($\varepsilon$) of the media through which the charges interact with each other has been simplified as the same. As a matter of fact, it may vary in different systems and even change dynamically with time, and in some circumstances this variation may have a pronounced effect on the interactions of the charges.

To summarize, anionic surfactants are the templating agents of the mesostructure of the AMS materials. The ionization degree of anionic surfactant, which can be tuned by the system acidity/alkalinity, can dramatically affect the structure of the resultant mesoporous silica through changing the organic/inorganic interface curvature. The following sections will show the versatility of this strategy in controlling the mesostructure.
4.1.2 Mesophase change of AMS systems using TMAPS as the CSDA

In the anionic surfactant/TMAPS system of the anionic-surfactant-templating route to mesoporous silica, the negatively charged headgroups of the anionic surfactants interact with the positively charged ammonium sites of TMAPS electrostatically. TMAPS is a kind of CSDA having a permanent positive charge, which is not affected by the conditions of synthesis system. Therefore, in the synthesis of AMS, the alkalinity affects the organic/inorganic interactions only through different ionization degree or charging state of anionic surfactants, as shown in Figure 10. We chose diprotic surfactant C_{14}GluA and monoprotic surfactant C_{16}ValS and C_{14}AS as the template for AMS, to investigate the effect of their ionization degree on the formation of mesostructures.

(1) Diprotic anionic surfactant as the template

Mesoporous silicas were synthesized using diprotic C_{14}GluA as the template and TMAPS as the CSDA, with addition of different amounts of NaOH. The samples are designated as GluA-TM-NaOH-x, where x represents the alkalinity, i.e. the molar ratio of NaOH/C_{14}GluA. Different mesophases have been obtained when x varied from 2.4 to 0.75, which can be confirmed from the XRD patterns (Figure 11) and HRTEM images (Figure 12).

Figure 11. XRD patterns of calcined mesoporous silica synthesized by using diprotic C_{14}GluA as the template and TMAPS as the CSDA with addition of different amount of base, NaOH. The compositions of the reaction mixtures are C_{14}GluA: TMAPS: TEOS: H_{2}O: NaOH = 1: 1.5: 15: 2000: x, where x = (a) 2.2, (b) 2.0, (c) 1.5, (d), 1.0 (e) 0.75 and (f) 0.5. The samples are designated as GluA-TM-NaOH-x.
GluA-TM-NaOH-2.2 and -2.0 are obtained in an alkaline system. GluA-TM-NaOH-2.0 is not a cubic phase, as no three-fold axis can be observed. Based on the tetragonal system the space group can be derived from the HRTEM images as $P4_2/mnm$. The space group shows significant amount of X-ray reflections in small angles, which make the XRD pattern difficult to resolve. Strong reflections has been calculated and indicated by arrows in the XRD pattern. It is a cage-type mesophase, with a high organic/inorganic interface curvature ($g = 1/3$).

GluA-TM-NaOH-1.5 is a cubic phase, and the space group is $Fd-3m$ deduced from the HRTEM images. Stacking faults can be easily found along the [1-11] direction, as indicated by the streaks in the Fourier diffractogram, which gives a diffused XRD pattern. Based on this space group the strongest X-ray reflection peak was assigned as 222 reflection. It is also a cage-type mesophase, having a high organic/inorganic interface curvature ($g = 1/3$).

Figure 12. HRTEM images and Fourier diffractograms of the calcined mesoporous silica GluA-TM-NaOH-2.0 (a, [001]), GluA-TM-NaOH-1.5 (b, [110]), GluA-TM-NaOH-1.0 (c), GluA-TM-NaOH-0.75 (d, [110], e, [100], f, [111]) and GluA-TM-NaOH-0.5 (g, h). The arrows indicates stacking faults of GluA-TM-NaOH-1.5 along the [1-11] direction.

When the alkalinity of the synthesis decreases to $x = 1.0$, however, a significant phase change occurs. The XRD pattern shows features of 2d-hexagonal $p6mm$, and the HRTEM image taken with the electron beam pa-
rallel to the channel axis shows well-ordered hexagonally arranged mesopores. Therefore it can be concluded that by decreasing the alkalinity, the organic/inorganic interface curvature is reduced and pore geometry becomes cylindrical ($g = 1/2$).

A novel bicontinuous cubic $Pn-3m$ structure could be obtained at a low alkalinity of the synthesis conditions (GluA-TM-NaOH-0.75, around pH neutral). It is named here AMS-10 of the AMS-$n$ family mesoporous materials. Reflection conditions can be derived from TEM images, as $0kl$: $k+l$ even, $00l$: $l$ even, $hkl$: none, $hhl$: none, and the space group is thus determined. The XRD peaks can be assigned as 110 and 111 reflections, having a spacing ratio of $\sqrt{3}/\sqrt{2}$. The bicontinuous cubic phase, as is well known, has a low organic/inorganic interface curvature, with $g$ in between 1/2 and 2/3. The structural features will be further discussed in the next section.

An expected lamellar phase does not appear when the synthesis system of the above system becomes less alkaline (more acidic). Instead, a worm-like mesophase (GluA-TM-NaOH-0.5) have been obtained, judged from the TEM images, and only one X-ray reflection peak can be observed at round 1° (2 theta). It is an extreme phase of this synthesis system, which is supposed to be formed by templating of neutral surfactant molecules.

![Figure 13. SEM images of GluA-TM-NaOH-x. a) $x=2.4$; b) $x=2.0$; c) $x=1.9$; d) & e) $x=1.5$; f) $x=0.75$.](image)

It can be concluded that by decreasing the alkalinity (or increasing the acidity) of the synthesis system, the resultant mesophase transformed from cage-type $P4_{2}/mnm$ and $Fd-3m$, to 2d-hexagonal $p6mm$, further bicontinuous $Pn-3m$ and finally a worm-like mesophase, showing an increased surfactant packing parameter $g$ and a decreased organic/inorganic interface curvature. In this process, the ionization degree of anionic surfactant becomes lower step by step, while the pH is buffered around neutral from weak basic to
weak acidic (initial pH before addition of silica source, 5–9), which gives rise to neglectable kinetic considerations, relatively. This change of meso-phase proves our proposed mechanism that the ionization degree of surfactant dominates the states of micelles and is the main factor for the determination and control of the mesostructure.

The morphologies of mesoporous silicas, as SEM images shown in Figure 13, are spheres at basic conditions, crystal-like at weakly basic and neutral conditions and irregular at weakly acidic conditions. For these crystal-like mesoporous materials, the crystals show $4/mmm$ and $m\overline{3}m$ point groups for the cage-type tetragonal and cubic mesophases, respectively, consistent with their space groups.

(2) Monoprotic anionic surfactant as the template

Here, AMS materials are synthesized using monoprotic anionic surfactants, $N$-palmitoyl valine sodium salt ($C_{16}$ValS) and myristic acid sodium salt ($C_{14}$AS), as the templates, and TMAPS as the CSDA, and the phase changes are presented to demonstrate the ionization degree controlling mechanism. The samples are denoted as ValS-TM-HCl-$x$ and C14S-TM-NaOH-$x$, where $x$ stands for the ratio of HCl/$C_{16}$ValS and NaOH/$C_{14}$AS, respectively. Their XRD patterns and TEM images are shown in Figure 14 and Figure 15.

![Figure 14](image-url) XRD patterns of mesoporous silica synthesized with monoprotic $C_{16}$ValS and $C_{14}$AS. The compositions of the reaction mixtures are $C_{16}$ValS: TMAPS: TEOS: H$_2$O: HCl = 1: 0.5: 7: 1978: $x$, where $x = 0.1$ (a, as-synthesized), 0.05 (b, calcined) and 0 (c, calcined) & $C_{14}$AS: TMAPS: TEOS: H$_2$O: NaOH = 1: 1: 7: 1389: $x$, where $x = 0$ (d) and 0.1 (e). The samples are designated as ValS-TM-HCl-$x$ and C14S-TM-NaOH-$x$, respectively.
The mesostructures of AMS materials prepared with C\textsubscript{16}ValS as the template are lamellar (ValS-TM-HCl-0.1), bicontinuous cubic \textit{Ia-3d} (ValS-TM-HCl-0.05) and 2d-hexagonal \textit{p6mm} (ValS-TM-HCl-0), respectively, derived from their XRD patterns and TEM images. The organic/inorganic interface curvatures of the mesophases are in an increasing order with an increase of alkalinity or a decrease of acidity of the synthesis conditions.

The mesostructure of AMS materials prepared with C\textsubscript{14}AS as the template are 2d-hexagonal \textit{p6mm} (C14S-TM-NaOH-0) and cage-type cubic \textit{Fd-3m} (C14S-TM-NaOH-0.1), respectively, showing lower and higher organic/inorganic interface curvature, when the system is in a weaker and stronger alkalinity conditions. From the TEM image the \textit{Fd-3m} shows perfect packing sequence without stacking faults, which gives XRD pattern of high quality.

Therefore, for monoprotic-anionic-surfactant templated mesoporous silicas, the phase change behavior with the alkalinity or the ionization degree of anionic surfactants is close to that of the diprotic-anionic-surfactant templating systems. The surfactant packing manner is highly dependent on the ionization degree of surfactant determined by the chemical equilibrium, which is sensitively affected by the alkalinity (or acidity) of the system.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure15.png}
\caption{HRTEM images and Fourier diffractograms of calcined mesoporous silica ValS-TM-HCl-0.05 (a, [311]), C14S-TM-HCl-0 (b) and C14S-TM-HCl-0.1 (c, [110]).}
\end{figure}

\subsection*{4.1.3 Mesophase change of AMS systems using APS as the CSDA}

APS is another commonly used CSDA in the synthesis of AMS materials. Compared with TMAPS, it has a variable charging state because of the presence of an amino group in a molecule (pK\textsubscript{b}~3.4). Therefore, besides the chemical equilibrium between neutral and ionized surfactant, the equilibrium between neutral and charged APS exists in the synthesis system, which makes it more complicated.

\begin{enumerate}
\item Diprotic anionic surfactant as the template
\end{enumerate}
First, diprotic anionic surfactant $C_{14}$GluA was used as the template and TMAPS as the CSDA to investigate the ionization degree controlled meso-phase change. Because APS is a kind of base, acid was added to the system for the control of ionization degree of surfactant and protonation of APS. The samples are designated as GluA-AP-HCl-x, where $x$ denotes the molar ratio of HCl/$C_{14}$GluA. Besides, APS/$C_{14}$GluA ratio was kept as 4. The XRD patterns and TEM images are shown in Figure 16 and Figure 17, respectively.

*Figure 16. XRD patterns of calcined mesoporous silica synthesized by using $C_{14}$GluA as template and APS as CSDA with addition of different amount of acid. The compositions of reaction mixtures are $C_{14}$GluA: APS: TEOS: H$_2$O: HCl = 1: 4: 15: 2000: $x$, where $x$ = (a) 0, (b) 1.6, (c) 2.4, (d) 2.8 and (e) 3.0. The samples are designated as GluA-AP-HCl-x.*

*Figure 17. HRTEM images and Fourier diffractograms of calcined mesoporous silica GluA-AP-HCl-0 (a), GluA-AP-HCl-1.6 (b, [110]), and GluA-AP-HCl-3.0 (c, [110]).*
Combined the results of XRD and TEM, the structures of the mesoporous silicas can be well determined as Pm-3n with modulations (GluA-AP-HCl-0), cage-type cubic Fd-3m (GluA-AP-HCl-1.6), 2d-hexagonal p6mm (GluA-AP-HCl-2.4 and -2.8) and bicontinuous cubic Pn-3m (GluA-AP-HCl-3), respectively, in the same order of increasing acidity or decreasing alkalinity of the system. The phase information is summarized in Table 4.

Table 4. Synthesis conditions of different mesophases from the C14GluA/APS system.

<table>
<thead>
<tr>
<th>x</th>
<th>(2C14GluA+HCl)/APS&lt;1</th>
<th>(2C14GluA+HCl)/APS&gt;1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Pm-3n with modulations</td>
<td>Fd-3m</td>
</tr>
<tr>
<td>Pore geometry</td>
<td>cage-type</td>
<td>cylindrical</td>
</tr>
<tr>
<td>Driving force</td>
<td>Protonation of APS</td>
<td>Ionization degree of surfactant</td>
</tr>
</tbody>
</table>

From Table 4 it can be inferred that the alkalinity/acidity affects the mesophase formation in a similar manner to that using TMAPS as the CSDA. More acidic or less alkaline conditions lead to formation of mesophases with lower organic/inorganic interface curvature. In the regions of base excess, i.e. (2C14GluA+HCl)/APS < 1, the addition of HCl into the synthesis system mainly makes APS protonated, and the ionization degree of surfactant is relatively high, which gives rise to cage-type mesophases. The formation of different cage type mesophases, modulated Pm-3n and Fd-3m, can be attributed to the counterion effect of protonated APS, an increase in concentration of which leads to a screening of the electrostatic interactions between mesocages (the concept of the mesocage and the mesocage packing mechanism will be discussed in section 4.3) and a change in their packing manner. After protonation of APS, more acid added to the synthesis system will protonate the surfactant anions, which makes the ionization degree of surfactant lower. Therefore, in the regions of (2C14GluA+HCl)/APS > 1, a dramatic change of mesophase was observed, from cage-type to 2d-hexagonal p6mm and further bicontinuous cubic Pn-3m.

Therefore, it can be concluded that, in the AMS synthesis system using APS as the CSDA, the concentration of protonated APS and ionization degree of surfactant are the factors to determine the mesophase. The mesophase change induced by the ionization degree of surfactant is much prominent, as it can dramatically affect the packing of surfactants.

(2) Monoprotic anionic surfactant as the template

The effect of ionization degree of monoprotic anionic surfactant on the mesophase formation was investigated, as the XRD patterns shown in Figure 18. N-lauroyl-L-alanine (C12AlaA) was used as the template, and the alkalinity of the synthesis system was raised to increase its ionization degree. The
mesophases obtained, are lamellar, bicontinuous cubic \( \text{Ia-3d} \) and 2d-hexagonal \( p6mm \), in succession, with decreasing the surfactant packing parameter \( g \) and decreasing the organic/inorganic interface curvature, which reconfirms the mechanism that the ionization degree of surfactant controls the mesophase formation.

\[ \text{Figure 18.} \text{ XRD patterns of mesoporous silica synthesized by using } C_{12}\text{AlaA as the template and APS as the CSDA with addition of different amount of base. The compositions of reaction mixtures are } C_{12}\text{AlaA: APS: TEOS: H}_2\text{O: NaOH = 1: 1: 7: 1500: } x, \text{ where } x = (a) 0, \text{ as made, (b) 0.2, as made, and (c) 0.8, calcined. The samples are designated as AlaA-AP-NaOH-x.} \]

4.1.4 Remarks on the ionization-degree controlled phase change

In the above discussions, the phase change mechanism of AMS by ionization degree of surfactant is widely examined and confirmed. The phase change is prominent, because the change of ionization degree of surfactant alters the state of surfactant, which is the main factor for the phase formation. It is one of the features how AMS differs from the cationic and non-ionic surfactant templating route, because in the latter cases, the states of surfac-
tant are rather stable as they are not easily affected by the synthesis conditions and are highly dependent on the molecular shape.

It is worth noting that, in the above discussions, we neglected the kinetics of the hydrolysis of silica source. This approximation was made because of the following reasons. First, the pH of the synthesis system is not harsh, and a mild pH within 5–9 was normally used, which is buffered by the carboxylate surfactant and/or APS. In these situations, the hydrolysis rates of TEOS are all slow. Besides, all the experiments were conducted following the same procedure, which makes the results comparable. Second, the strong interaction between surfactant and CSDA makes the self-assembly of both surfactant and CSDA very quick, much quicker than the hydrolysis rate of TEOS. As the hydrolysis of TEOS proceeds, the organic/inorganic assembling takes place. Therefore, the kinetics of hydrolysis of TEOS does not affect prominently the assembly and thus the resultant mesophase.

It is also worth noting the phase selectivity. The ionization degree of surfactant accounts for the change of mesophase of different types, e.g. mesophase change from lamellar to bicontinuous, 2d-hexagonal and cage-type, through the change of organic/inorganic interface curvature. However, it cannot explain why the structure is $Pn-3m$ but not $Ia-3d$, or why the structure is $Fd-3m$ but not $Fm-3m$, because all these phases have the similar organic/inorganic interface curvatures. Discussions on these phase selectivity will be presented in the following several sections (Section 4.2 and 4.3).

4.2 A novel bicontinuous cubic $Pn-3m$ and its inverse structure

4.2.1 Synthesis strategy and 3d-reconstruction of bicontinuous cubic $Pn-3m$

Bicontinuous cubic phases include $Ia-3d$, $Pn-3m$ and $Im-3m$, which have been discovered for long in liquid crystal phases. In mesoporous materials, $Ia-3d$ structure has been discovered at the very beginning of the research, e.g. MCM-48. Bicontinuous cubic $Im-3m$ was also reported as the “plumber’s nightmare”, though further reconstruction needs to be done to confirm the pore connectivity. In this work, we synthesized a novel bicontinuous cubic $Pn-3m$ mesoporous silica structure using anionic surfactant templating system.

It has been proposed that, the amount of water accommodated in the G ($Ia-3d$), D ($Pn-3m$), and P ($Im-3m$) phases increases accordingly in liquid crystal phases. This statement provides a possible route for the rational synthesis of bicontinuous cubic phases.
It can be inferred that in a silicatropic liquid crystal (SLC) phase of surfactants, the selectivity of bicontinuous cubic phases depends on the silica accommodation capability, which is decided by the nature of a surfactant, i.e. the hydrophilic/hydrophobic balance. For surfactants having only one head-group per molecule, they easily afford bicontinuous cubic $Ia-3d$ structure. Such surfactants include CTAB, $C_{16}ValS$, $C_{12}AlaA$, etc. Therefore, by enlarging the headgroups of surfactant, bicontinuous cubic phases like $Pn-3m$ and $Im-3m$ could be possibly obtained.

In our strategy, a glutamic acid derived diprotic anionic surfactant, $C_n$GluA, was employed as the template for mesoporous materials. The organic/inorganic interface curvature of the mesoporous silicas was by the means of decreasing the ionization degree of surfactant. As a result, a novel bicontinuous cubic $Pn-3m$ mesoporous silica AMS-10 has been prepared.

Table 5. Crystal structure factors extracted from HRTEM of calcined AMS-10 ($a = 9.6$ nm).

| $h$ | $k$ | $l$ | $|h|^2 + |k|^2 + |l|^2$ | $d$ [nm] | Amplitude | Phase |
|-----|-----|-----|----------------|----------|-----------|-------|
| 1   | 1   | 0   | 2              | 6.80     | 100.00    | $\pi$ |
| 1   | 1   | 1   | 3              | 5.55     | 57.09     | 0     |
| 2   | 0   | 0   | 4              | 4.81     | 13.13     | 0     |
| 2   | 1   | 1   | 6              | 3.92     | 3.40      | $\pi$ |
| 2   | 2   | 0   | 8              | 3.40     | 0.79      | $\pi$ |
| 2   | 2   | 1   | 9              | 3.20     | 0.57      | 0     |
| 3   | 1   | 0   | 10             | 3.04     | 0.42      | $\pi$ |
| 3   | 1   | 1   | 11             | 2.90     | 0.06      | 0     |
| 2   | 2   | 2   | 12             | 2.77     | 0.20      | $\pi$ |
| 3   | 2   | 1   | 14             | 2.57     | 0.13      | 0     |
| 4   | 0   | 0   | 16             | 2.40     | 0.10      | 0     |
| 3   | 2   | 2   | 17             | 2.33     | 0.10      | $\pi$ |
| 3   | 3   | 0   | 18             | 2.27     | 0.07      | 0     |
| 4   | 2   | 0   | 20             | 2.15     | 0.01      | $\pi$ |
| 4   | 3   | 3   | 34             | 1.65     | 0.05      | 0     |
| 4   | 4   | 2   | 36             | 1.60     | 0.02      | 0     |
| 7   | 1   | 0   | 50             | 1.36     | 0.01      | 0     |
| 6   | 3   | 3   | 51             | 1.35     | 0.01      | 0     |

The XRD pattern and TEM images of the calcined AMS-10 can be found in Figure 11 and 12, respectively. The symmetry can be determined according to the reflection conditions derived from the Fourier diffractograms of the TEM images. To investigate the pore connectivity, the 3d-reconstruction was carried out by electron crystallography, combing the data of TEM and nitrogen adsorption.

Crystal structure factors have been extracted from HRTEM of calcined AMS-10, as shown in Table 5, with both amplitudes and phases presented. The electrostatic potential density map of AMS-10 was obtained by taking inverse Fourier summation of these crystal structure factors. With a silica density of about 2.2 g/cm$^3$ and a pore volume of 0.65 cm$^3$/g derived from
nitrogen adsorption data, the 3d pore structure of AMS-10 was determined and shown in Figure 19.

From this result, it can be conclude that AMS-10 has a bicontinuous structure composed of an enantiomeric pair of 3d mesoporous networks that are interwoven with each other. Each network, which is divided by a diamond (D) surface, consists of tetrahedral connection of mesopores. (For its analog structures, \( Ia-3d \) and \( Im-3m \), refer to section 2.4)

![Figure 19. 3D structure of a) the bicontinuous cubic AMS-10 (as derived from electron crystallography), b) the D surface, and c) the 3D networks of double diamond structure divided by the D surface. They show a 2x2x2 unit cell.](image)

4.2.2 Remarks on the synthesis of bicontinuous cubic \( Pn-3m \)

The synthesis of bicontinuous cubic \( Pn-3m \) structure was only achieved from templating systems using diprotic anionic surfactants. In these systems, the occurrence of \( Pn-3m \) structure was found in between the 2d-hexagonal phase \( p6mm \) and a worm-like phase. However, if monoprotic anionic surfactant was used, it can be seen from section 4.1 that the bicontinuous cubic phase was \( Ia-3d \), the occurrence of which is in between \( p6mm \) and lamellar. These differences confirm that the selectivity of specific bicontinuous cubic phase depend on the nature of surfactant, \( i.e. \) water accommodation capability, which is determined by the molecular structure of the surfactant.

Based on these considerations, it is reasonable to infer that by further increasing the headgroups of anionic surfactant, a bicontinuous cubic \( Im-3m \) could be possibly synthesized by the AMS route. Also, these bicontinuous cubic phases could be found in other synthesis systems, for example cationic or nonionic surfactant templating systems, if proper geometry of surfactant is selected and proper method is adopted to adjust the organic/inorganic interface curvature.
4.2.3 Inverse structure of bicontinuous $Pn$-$3m$

The hard template nanocasting method is a versatile way to synthesize materials with controlled chemical compositions and structures. And as has been reviewed in section 2.5, nanocasting is a method eligible to provide additional structural information of the host mesoporous materials. In this work, we will synthesize the inverse structure of bicontinuous cubic $Pn$-$3m$ by replicating it into mesoporous Co$_3$O$_4$ material, and find additional structural properties of host AMS-10 by this means.

(1) Synthesis of AMS-10 with different pore sizes

![Figure 20.](image)

*Figure 20.* XRD patterns (A), Nitrogen adsorption/desorption isotherms (B) and the pore size distributions (C) of calcined AMS-10-$x$ ($x$: HCl/C$_{14}$GluAS molar ratio). The mol compositions are: C$_{14}$GluAS: TMAPS: TEOS: H$_2$O: HCl 1: 1.5: 15: 2000: $x$. The reaction was conducted at 80°C for 2 days. The isotherms of AMS-10-0.44, 0.45 and 0.48 were moved vertically by 200, 400 and 600 cm$^3$ g$^{-1}$, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit cell parameter (nm)</th>
<th>$S$ (m$^2$g$^{-1}$)</th>
<th>$V$ (cm$^3$g$^{-1}$)</th>
<th>Pore diameter (nm)</th>
<th>Wall thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS-10-0.42</td>
<td>9.0</td>
<td>649</td>
<td>0.87</td>
<td>5.1</td>
<td>1.3</td>
</tr>
<tr>
<td>AMS-10-0.44</td>
<td>9.5</td>
<td>624</td>
<td>0.90</td>
<td>5.5</td>
<td>1.2</td>
</tr>
<tr>
<td>AMS-10-0.45</td>
<td>9.8</td>
<td>640</td>
<td>0.94</td>
<td>5.8</td>
<td>1.1</td>
</tr>
<tr>
<td>AMS-10-0.48</td>
<td>11.0</td>
<td>640</td>
<td>1.04</td>
<td>6.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Mesoporous silica materials AMS-10 with different pore sizes were synthesized by fine tuning the ionization degree of diprotic surfactant C$_{14}$GluAS. Here, C$_{14}$GluAS was produced by neutralization of C$_{14}$GluA with equivalent amount of NaOH. The reaction was carried out at a higher temperature (80°C). Therefore, the absolute acidity may differ from previous syntheses.
It can be seen from Figure 20 and Table 6 that by increasing the HCl/C14GluNa molar ratio from 0.42 to 0.48, all the obtained materials have bicontinuous cubic $Pn-3m$ structure. The AMS-10 obtained shows enlarging mesopore size from 5.1 nm to 6.7 nm. In the meanwhile, the wall thickness of the AMS-10 materials decreases from 1.3 nm to 1.1 nm.

(2) Inverse replication of AMS-10

The AMS-10 was used as the hard template, and non-siliceous Co$_3$O$_4$ mesoporous materials with inverse structure of AMS-10 were obtained by nanocasting method, denoted as Co$_3$O$_4$-AMS-10-x. Their XRD patterns are shown in Figure 21.

![Figure 21. XRD patterns of mesoporous Co$_3$O$_4$ templated by AMS-10-x.](image)

An X-ray reflection peak with low intensity is observed from each XRD pattern, which can be reasonably assigned to the 110 reflection, showing the d-spacing close to that of the silica template. These peaks can be explained as the X-ray reflections from the mesoporous Co$_3$O$_4$ that is obtained by replication of two sets of the bicontinuous mesopore networks, which shows the same unit cell dimensions as the silica template. The low intensity of the X-ray reflection indicates that replication of two sets of bicontinuous mesopore network by Co$_3$O$_4$ occurs only partially. Replication of only one set of the bicontinuous mesochannels may also occur, which doubles the unit cell dimensions and therefore the X-ray reflections shift to a much smaller angle.
The nitrogen adsorption/desorption isotherms and pore size distributions of AMS-10 Co₃O₄ materials are shown in Figure 22. The isotherms are of type IV and have typical hysteresis loops showing the features of mesoporous materials. The pore sizes are bimodal-type, distributed within the ranges of 2–5 nm and 5–15 nm, respectively. Considering the porous properties of host AMS-10 materials, it is reasonable that the pore size distribution of mesoporous Co₃O₄ within 2–5 nm is attributed to replication of both sets of the bicontinuous mesopores of AMS-10. On the other hand, the pore size of mesoporous Co₃O₄ within 5–12 nm is much larger than the wall thickness of silica template and close to twice of the wall thickness plus pore diameter of silica template (7–8 nm), which might be attributed to the replication of only one set of the bicontinuous mesochannels. Therefore, it can be concluded that, within the full range of pore size of AMS-10, Co₃O₄ replicates both one set and two sets of the bicontinuous mesochannels.

Figure 22. Nitrogen adsorption/desorption isotherms (A) and pore size distributions (B) of the mesoporous Co₃O₄ replicas templated by AMS-10-x. The isotherms of Co₃O₄-AMS-10-0.44, 0.45 and 0.48 were moved vertically by 100, 200 and 300 cm³ g⁻¹, respectively.

The replication is further demonstrated by TEM observations as images shown in Figure 23. It is clear that only one set of the nonintersecting channel network was replicated on the edge of the Co₃O₄ replica, but in the thick areas both bicontinuous channel networks were replicated, which is coincide with the nitrogen adsorption experiment.
In the process of inverse replication, the inorganic precursor is infilt-
trated into the two sets of the bicontinuous mesochannels, which is further
crystallized by thermal treatment. The precursor in each of the bicontinuous
mesochannels nucleates and grows independently, accompanied with a dra-
matic mass transfer due to the insufficient amount of the precursor. As a
result, a replication of only one set of the bicontinuous mesochannels could
be achieved. However, if the inorganic precursor is able to diffuse between
the two bicontinuous mesochannels, the oxides could fill the two biconti-
nuous mesochannels in the same region during crystallization, leading to a
replication of both sets of the bicontinuous mesochannels. Therefore, the
results of replication of AMS-10 by Co$_3$O$_4$ indicate the existence of effective
connections between two bicontinuous mesochannels.

4.2.4 Remarks on the structure of bicontinuous cubic $Pn\bar{3}m$

It has been shown that in the inverse replication of AMS-10 with different
pore sizes, both one set and two sets of bicontinuous mesochannels are repli-
cated. Replication of both sets of bicontinuous mesochannels was also observed when using KIT-6 of $Ia$-$3d$ structure as the hard template. It has been proposed that the disordered micropores formed by polyethyl oxide (PEO) of surfactant and ordered complimentary micropores (Figure 24) in the silica wall account for the diffuse of guest precursors within adjacent mesochannels and the consequent replication of two sets of mesochannels.\[89,91\]

**Figure 24.** Ordered complementary pores present in KIT-6, connecting the two mesopore networks. Adopted from reference [91].

Different from KIT-6, AMS-10 is prepared by using anionic surfactant as the template. As a result, no disordered micropores are present in the silica walls because no PEO are involved in the synthesis of host mesoporous materials. Therefore, one possibility is the presence of ordered complimentary micropores in the thinnest parts of the silica wall of $Pn$-$3m$ bicontinuous structure, which leads to the diffuse of $Co_3O_4$ precursors within different set of mesochannels, and therefore two sets of bicontinuous mesopores are replicated.

### 4.3 Formation of cage-type mesophases: The mesocage model

The anionic-surfactant-templating route to mesoporous silica shows advantages that the organic/inorganic interaction can be well defined and tuned and diverse mesophases can be obtained in one synthesis system. Therefore, it provides a good candidate for the research on mesophase formation. In this work, a full-scaled synthesis-field diagram of AMS was investigated. On this basis the formation mechanism and the structural relationship of different mesophases, especially cage-type mesophases, have been further discussed in details.
4.3.1 The C\textsubscript{14}GluA/NaOH/TMAPS synthesis-field diagram

A diprotic C\textsubscript{14}GluA was chosen as the referenced structure directing agent, which creates the possibility of forming various cage-type mesophases with highly curved organic/inorganic interface curvatures as well as mesophases with reduced curvatures. The key compositions have been determined as C\textsubscript{14}GluA, NaOH and TMAPS, tuning the ratios of which a synthesis-field diagram was completed. The determination of each mesophase was based on its XRD and HRTEM. The diagram is shown in Figure 25, and it can be seen that phases are present in it including bicontinuous cubic \textit{Pn}-3\textit{m}, 2d-hexagonal \textit{p6mm}, cage-type cubic \textit{Fd}-3\textit{m}, \textit{Pm}-3\textit{n}, \textit{Fm}-3\textit{m} and cage-type tetragonal \textit{P4\textsubscript{2}/mmn}, etc. Table 7 summarizes the synthesis conditions for each mesophase.

The formation of bicontinuous cubic \textit{Pn}-3\textit{m} and 2d-hexagonal \textit{p6mm} has been discussed extensively, and our focus shifts then to the cage-type mesophases, which have been well located in the synthesis-field diagram in Figure 25.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{synthesis-field-diagram.png}
\caption{Synthesis-field diagram (mole fraction) of the C\textsubscript{14}GluA/NaOH/TMAPS system.}
\end{figure}
Table 7. Synthesis conditions of the mesophases in the C_{14}GluA/NaOH/TMAPS system.

<table>
<thead>
<tr>
<th>Mesophase</th>
<th>Mesopore type</th>
<th>pH[^a]</th>
<th>NaOH/ C_{14}GluA</th>
<th>TMAPS/ C_{14}GluA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pn3m</td>
<td>bicontinuous</td>
<td>5.0–5.2</td>
<td>0.45–0.62</td>
<td>0.84–3.8</td>
</tr>
<tr>
<td>p6mm</td>
<td>cylindrical</td>
<td>5.2–5.6</td>
<td>0.62–0.86</td>
<td>0.35–3.8</td>
</tr>
<tr>
<td>Fd3m</td>
<td>micellar cubic</td>
<td>5.6–6.2</td>
<td>0.86–1.25</td>
<td>1.1–4.5</td>
</tr>
<tr>
<td>undefined</td>
<td>–</td>
<td>6.2–7.4</td>
<td>1.25–1.7</td>
<td>1.6–3.8</td>
</tr>
<tr>
<td>Pm3n</td>
<td>micellar cubic</td>
<td>6.1</td>
<td>1.16</td>
<td>1.0</td>
</tr>
<tr>
<td>P4_3/mnm</td>
<td>micellar tetragonal</td>
<td>6.7</td>
<td>1.56</td>
<td>1.2</td>
</tr>
<tr>
<td>Fm3m</td>
<td>micellar cubic</td>
<td>7.4–11.0</td>
<td>1.7–2.7</td>
<td>1.6–3.3</td>
</tr>
</tbody>
</table>

[^a] The pH of the reaction solution was measured at 70°C before the addition of TMAPS and TEOS.

The XRD patterns, TEM and SEM images of the typical cage-type phases are displayed in Figure 26. All the materials have highly ordered mesostructures, which can be inferred from the well resolved XRD patterns and the high order of large domains in TEM images. The reflection conditions as shown in the diffractograms reveal and confirm the space groups of each phase. The XRD patterns, except for that of P4_3/mnm structure, are of high quality showing typical reflection peaks for their symmetries, indicating that the phases are fairly pure. The purity of the P4_3/mnm has been confirmed by the TEM observations and crystal morphology, given that the difficulty of XRD characterization of the structure has been realized (Section 4.1.2). The morphologies of the samples observed from the SEM images are crystal-like, and have m-3m symmetry for the Fd-3m and Pm-3n cubic phases and 4/mmm symmetry for the P4_3/mnm tetragonal phase. The polyhedron crystal-like morphology of the Fm-3m cubic phase does not fit m-3m point group symmetry, which can be explained by twinning that is commonly observed in face-centered cubic structures.[57]
Figure 26. (a) XRD pattern, (b) HRTEM image (inset: Fourier diffractogram) and (c) SEM image of the cage-type mesoporous silicas having the space group of cubic $Fd-3m$ (A, C$_{14}$GluA/NaOH/TMAPS 0.284: 0.334: 0.382), $Pm-3n$ (B, C$_{14}$GluA/NaOH/ TMAPS 0.317: 0.367: 0.317), $P4_{2}/mnm$ (C, C$_{14}$GluA/NaOH/TMAPS 0.267: 0.417: 0.317) and $Fm-3m$ (D, C$_{14}$GluA/NaOH/TMAPS 0.200: 0.400: 0.400).

An undefined mesophase was found which is located in between the structures of $Fm-3m$, $P4_{2}/mnm$ and $Fd-3m$ in the synthesis-field diagram, around the composition point C$_{14}$GluA/NaOH/TMAPS 0.2: 0.3 : 0.5. The XRD patterns and TEM images are shown in Figure 27. The structure is
unstable to thermal treatment and only one broad X-ray reflection peak remains after calcinations with decreased intensity. The TEM images reveal it shows the short-distance ordering, and the long-distance ordering is very poor. We propose that the formation of this undefined phase is a result of the mismatch of kinetics of self-assembly and hydrolysis of silica source. This phase is obtained at a neutral pH condition (pH 6.2–7.4), and the hydrolysis of TMAPS and TEOS is much slower within this range of pH than required to match the kinetics of self-assembly of organic/inorganic species. Therefore, no highly ordered mesophases have been obtained.

Figure 27. XRD pattern and (b, c) HRTEM images of the mesophase formed from the synthesis system of C$_{14}$GluA/NaOH/TMAPS 0.233:0.333:0.433.

In the compositions zones like $\alpha$, $\beta$ and $\gamma$, the mesophases obtained are mixtures of the adjacent mesophases. Taking zone $\alpha$ for example, the resultant mesoporous silica is a mixture of particles having structures of cubic $Pm-3n$, $Fm-3m$ and tetragonal $P4_2/mnm$. Figure 28 shows their TEM images, respectively, confirming the existence of these structures.

Figure 28. HRTEM images of the mesophase formed from the synthesis system C$_{14}$GluA/NaOH/TMAPS 0.267:0.367:0.367. It shows a coexistence of cubic (a) $Pm-3n$, (b) $Fm-3m$ and (c) tetragonal $P4_2/mnm$.

In the composition zones like $\delta$, $\epsilon$ and $\zeta$ shown in Figure 25, highly ordered mesostructures could not be formed because the mole fraction of NaOH, C$_{14}$GluA or TMAPS, respectively, is too high. Taking zone $\delta$ for example, the resultant mesostructure is disordered, as the XRD pattern and TEM image shown in Figure 29 indicates. The mesoporous silica was obtained at a high alkalinity (NaOH/C$_{14}$GluA = 2.5, pH higher than 11.0). In
this condition, the hydrolysis of silica source is quick, which is beyond the kinetics of self-assembly of organic/inorganic species. As a result, the micelles do not have the chance to arrange in a close way which is the time-consuming step for this system.

![Figure 29. (a) XRD pattern and (b) HRTEM image (inset: Fourier diffractogram) of the mesophase formed from the synthesis system C\textsubscript{14}GluA/NaOH/TMAPS 0.200:0.500:0.300.](image)

### 4.3.2 Discussions on the synthesis-field diagram

The phase fields are strip-like, lie in the sector zones employing C\textsubscript{14}GluA/NaOH/TMAPS 0:0:1 as the vertex. It indicates that the determining factor of the mesophase formation is the ionization degree of the surfactant (NaOH/C\textsubscript{14}GluA); the effect of the amount of TMAPS in the synthesis gel on the mesophase formation is not prominent. The bicontinuous \( Pn-3m \) and 2d-hexagonal \( \text{p6mm} \), which show a low organic/inorganic interface curvature and the bicontinuous/cylindrical mesopore geometry, are formed in systems with a low ionization degree of surfactant showing an initial pH range of as low as 5.0–5.6. The cage-type mesophases with high organic/inorganic interface curvatures are formed in systems with a high ionization degree of surfactant showing a relatively high pH of 5.6–11.0. This highlights the effect of the ionization degree of surfactant on the formation of mesophase, which is highly consistence with our previous discussions.

The ionization degree of surfactant cannot explain the formation of cage-type mesophases, as they are all formed by packing of spherical micelles (\( g = 1/3 \)). However, as many cage-type mesophases could be well located in the synthesis-field diagram of AMS, a reliable mechanism could be reasonably derived from their different synthesis conditions. The capability of forming diverse mesophases in one synthesis system of AMS using a diprotic anionic surfactant as the template paves a way to the understanding of cage-type formation mechanism.
4.3.3 Formation of cage-type mesophases: The mesocage model

Examples of the packing manner of spherical micelles in a cage-type mesostructure are visualized in Figure 30. It has been widely accepted that there are only one type of spheres in the structures of \(Im-3m\), \(P6_3/mmc\) and \(Fm-3m\), etc. However, there are two or more than two types of spheres with different sizes in the structures of \(Fd-3m\), \(Pm-3n\) and \(P4_2/mnm\), etc.\(^6,8,56,57\)

![Figure 30. Packing model of (A) \(Pm-3n\), (B) body centered cubic \(Im-3m\), (C) hexagonal close packing \(P6_3/mmc\) and (D) cubic close packing \(Fm-3m\).](image)

Among these structures, \(Fm-3m\) and \(P6_3/mmc\) are commonly seen in hard-sphere packing systems, in which close packing is the key factor to determine the packing manner of spheres. Their maximum porosity in theory is both 0.7405. The others are not close packed systems found usually in soft-matters e.g. liquid crystals, and the packing manner of spheres is the result of a compromise between the minimization of surface area and close packing.\(^{125–127}\)

Most of phases are present in our synthesis-field diagram of AMS, except for body-centered cubic \(Im-3m\) and 3d-hexagonal \(P6_3/mmc\). It provides possibilities to explain when close packing or minimization of surface area dominates the packing manner of spheres, and how they affect their packing, from the perspective of chemistry.

Our discussion is based on electric double layer of the interfacial chemistry.\(^{128}\) As shown in Figure 31, a charged surface of solid is immersed into an ionic liquid. This surface charge creates an electrostatic field which then
affects the ions in the bulk of the liquid. This electrostatic field creates a layer of counter charge, and thus screens the electric surface charge. Some of the counterions might specifically adsorb near the surface and build an inner sublayer, or the so-called Stern layer. The outer part of the screening layer is usually called the diffuse layer. The stern layer is within the boundary of slipping plane which separates mobile fluid from fluid that remains attached to the surface.

Figure 31. A simple model of a Stern layer.

As shown in Figure 32, in the formation of cage-type mesostructures of AMS system, anionic surfactants form micelles, which can be regarded as a negatively charged spherical surface. In the outside of this surface, to balance the negative charges, positively charged CSDA distributes in both the Stern layer in which immobile CSDA cations are specifically and tightly bonded to the surface and the diffuse layer in which mobile CSDA cations weakly interact with the charged surface. Therefore, the unit which is comprised of the micelle and the inorganic species in the Stern layer, and is the building block of cage-type mesostructure, and we call it a “mesocage”. The mesocages are then packed by certain means with hydrolyzed TEOS to form the mesostructure. In this model, the “mesocage” acts as a “brick” and the hydrolyzed TEOS acts as “mortar”, and the interactions between the “bricks” dominate the structure of the formed composite matrix.
Figure 32. Different charging states of mesocage: A, The mesocage is mildly negatively charged when the surfactant micelle shows low charge density; B, The mesocage is highly negatively charged when the micelle shows high charge density. The different charging state leads to different interactions between the mesocages and different packing manners.

The overall charging of a mesocage is negative, because the positive charges in the Stern layer could not balance the negative charges of the micelles, which could only be achieved at an infinite distance. The electrostatic repulsive interaction between the mesocages changes with the ionization degree of surfactant or the charging state of the micelles and further determines the packing manner of these mesocages. As described in Figure 32, when the charge density of the micelles is low, the mesocages are mildly charged, and the mesocage/mesocage electrostatic interaction is weak; on the contrary, when the charge density of the micelles gets higher, the mesocages are highly charged, and the mesocage/mesocage electrostatic interaction gets stronger.

Figure 33. Locations of different cage-type mesophases in the synthesis-field diagram.
The locations of cage-type mesophases are displayed in Figure 32, which is reproduced from Figure 25. The red lines indicate zones of surfactant with different ionization degree and therefore different charging density of the spherical micelles. It can be inferred that, in the mildly alkaline zones of the diagram, the ionization degree of surfactant is relatively low, and therefore the mesocages are moderately charged and the interactions are weak; cubic $Pm-3n$ and $Fd-3m$ are formed by packing of these mesocages. If the ionization degree of the surfactant gets higher at more alkaline conditions, the mesocages are highly charged because of the high charge density on the micelle surfaces, and therefore the mesocage/mesocage interactions are strong; tetragonal $P4_2/mnm$ can be found in these zones of the diagram. If the reaction is carried out under even stronger alkaline conditions, the strong mesocage/mesocage interactions caused by the highly charged mesocages give rise to a face-centered close-packed cubic $Fm-3m$ mesophase.

Therefore, it can be inferred that the charging state of the mesocages or the mesocage/mesocage interaction is the determining factor of the packing manner of the mesocages, which leads to different cage-type mesostructures. Therefore, it is clear that the mesocage/mesocage interaction determines the favored formation conditions of a specific cage-type mesophase.

It is worthy to note the effect of the concentration of TMAPS on the formation of cage-type mesophases. It can be seen from Figure 33 that at a similar ionization degree of surfactant, the mesophase differs due to the variation in concentration of TMAPS, e.g. the formation of $Fd-3m$ and $Pm-3n$. A high concentration of TMAPS in the synthesis system gives rise to a more charged stern layer, which screens more negative charges of the micelles and reduces the mesocage/mesocage interactions. Therefore, in this sense, the concentration of TMAPS counterions affects the packing of mesocages.

4.3.4 Remarks on the mesocage model

Conclusions on the formation of cage-type mesophases can be drawn as follows.

1. The charging of a mesocage determines its softness. A mesocage with high charging density can be regarded as a “hard sphere”, the packing of which is determined by close packing, leading to formation of $Fm-3m$ or possibly $P6_3/mmc$. When a mesocage has a low charge density, it can be regarded as a “soft sphere”, the packing of which is determined by a compromise between close packing and minimization of surface area. In this case, $Fd-3m$, $Pm-3n$ and $P4_2/mnm$ are favored.

2. In the “soft sphere” packing, the electrostatic repulsive interaction between mesocages determines their packing manner. When the interaction between mesocages is weak, $Fd-3m$ and $Pm-3n$ are favored to form; while when the interaction becomes strong, $P4_2/mnm$ is favored.
Figure 34. The kinetic control of cage-type structures of AMS. Adapted from reference [8].

The mesocage packing model is consistence with the results of earlier researches on the packing of latex spheres with identical sizes.\textsuperscript{[129]} The authors claimed that the packing manner of latex hard spheres is affected by the solid concentration, dipole and its softness which is determined by the charging state. Different from their system, the structures of mesoporous materials are formed from a “soft” system. Therefore, more abundant mesophases can be formed including $Fd-3m$, $Pm-3n$ and $P4_{2}/mmn$, which have several types of micelles with different sizes in a single phase.

In the earlier work, researchers found the kinetics controlled mesophase transformation of AMS materials, as shown in Figure 34.\textsuperscript{[8]} By increasing the addition time interval of APES and TEOS (APES-$t$-TEOS), different cage-type mesophases can be obtained, in an order of $Fd-3m$, $P4_{2}/mmn$, $Pm-3n$ and $Fd-3m$. The authors did not give clear explanations on the phase transformation. However, based on our model a reasonable explanation to the phase change could be given. It is known that the rate of hydrolysis and condensation of organosilane (APES) is lower than TEOS, and a larger value of the delayed time (APES-$t$-TEOS) makes pre-hydrolyzed APES and thus facilitates the co-condensation of APES and TEOS, which leads to a Stern layer with lower positive charge density and therefore larger mesocage/mesocage interactions. However, the further elongation of the delayed time results in a self-condensation of APES, which leads to a higher positive charge density of the Stern layer and therefore lower mesocage/mesocage
interactions. The change of mesocage interactions in this process (first strengthened and then weakened) explains well of the change in the mesophase.

4.4 Structural control by molecular design route

The effect of the molecular geometry on the resultant mesophase has been reviewed in section 2.4. In this section, rational syntheses of AMS mesoporous silica materials are achieved by a molecular design route. The effect of the geometry of surfactant and CSDA on the formation of mesostructures are investigated and discussed in details. Also, a thick-walled AMS mesoporous silica material is designed by this route.

4.4.1 Effect of the geometry of headgroup of surfactant

As the definition of the surfactant packing parameter \( g = \frac{V}{a_0h} \), the geometry of surfactants can affect the packing manner in a micelle. The effective headgroup area and alkyl chain length are two eligible ways.

Figure 35 shows the XRD patterns of mesoporous silica synthesized with anionic surfactants bearing headgroups of different sizes as the template and APS and TMAPS as the CSDA, respectively. Table 8 lists the porous properties of the materials. For the purpose of comparison, the alkyl chain length has been controlled as the same for each group.

![Figure 35. XRD patterns of the mesoporous silica synthesized with surfactant of different head groups as the template and APS (I) or TMAPS (II) as the CSDA. The surfactants used in the syntheses are: (a) C\(_{12}\)AA, (b) C\(_{12}\)AlaA, (c) C\(_{12}\)GluA, (d) C\(_{14}\)AS, (e) C\(_{14}\)GlyS, and (f) C\(_{14}\)GluS, respectively. Sample (a) is as-synthesized and the others are calcined.](image-url)
Table 8. Mesostructure and porous properties of the calcined mesoporous silicas synthesized with surfactant of different head groups as the template and APS or TMAPS as the CSDA.

<table>
<thead>
<tr>
<th>CSDA</th>
<th>Surfactant</th>
<th>Mesostructure</th>
<th>Surface area (m²/g⁻¹)</th>
<th>Pore Volume (cm³/g⁻¹)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS</td>
<td>C₁₂AA</td>
<td>Lamellar</td>
<td>654</td>
<td>0.44</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>C₁₂AlaA</td>
<td>2d-hexagonal $p6mm$</td>
<td>963</td>
<td>0.69</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>C₁₂GluA</td>
<td>Modulated cubic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMAPS</td>
<td>C₁₄AS</td>
<td>2d-hexagonal $p6mm$</td>
<td>520</td>
<td>0.53</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>C₁₄GlyS</td>
<td>2d-hexagonal $p6mm$</td>
<td>502</td>
<td>0.42</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>C₁₄GluS</td>
<td>3d-hexagonal $P6₃/mmc$</td>
<td>501</td>
<td>0.32</td>
<td>2.3</td>
</tr>
</tbody>
</table>

These mesophases have been determined by the combination of XRD and TEM as lamellar, 2d-hexagonal ($p6mm$) and cage-type cubic (modulated $Pm-3n$), when using C₁₂AA, C₁₂AlaA and C₁₂GluA as the template and APS as the CSDA, respectively, and 2d-hexagonal ($p6mm$), 2d-hexagonal ($p6mm$) and cage-type $P6₃/mmc$, when using C₁₄AS, C₁₄GlyS, and C₁₄GluS as the template and TMAPS as the CSDA, respectively.

It is evident that the geometry of the headgroup of surfactant increases in an order of carboxylic acid $<$ alanine $<$ glutamic acid, or carboxylate $<$ glycinate $<$ glutamate. The mesophases obtained by these surfactants with increasing headgroup areas have increasing organic/inorganic interface curvature, and the pore geometry changes dramatically from lamellar to cylindrical and further cage-type.

It is worthy to note that, the pore sizes of mesoporous silica materials templated by the surfactants with the same alkyl length are almost the same, indicating the effect of alkyl length of surfactant on the properties of mesostructures. As an exception, material prepared by glutamate surfactant shows a smaller pore size due to the re-configuration of the alkyl chains in the spherical micelle. (Section 4.5.2)

4.4.2 Effect of the alkyl length of surfactant

The alkyl chain of surfactant is the pore-creating agent (porogen), and therefore its length directly affects the pore size of the resultant mesoporous silica. Also, it can be easily inferred that the longer the alkyl length, the larger the surfactant packing parameter. Therefore, longer alkyl chain of surfactant leads to mesoporous silica with larger mesopores and lower organic/inorganic interface curvature.

Mesoporous silicas were synthesized by using fatty acid sodium salts CₙAS (n = 12–18) as the template to demonstrate the effect of the alkyl length. The XRD patterns are shown in Figure 36 and the porous properties are listed in Table 9.
As determined by XRD and TEM, the structures of mesoporous silica synthesized with fatty acid with increasing alkyl chains are cage-type cubic, 2d-hexagonal \( p6mm \), 2d-hexagonal \( p6mm \) and lamellar, respectively. The longer alkyl chain facilitates the formation of mesophase with lower organic/inorganic interface curvature. The pore sizes are increasing from 3.2 nm to 5.2 nm as the alkyl length rises.

Figure 36. XRD patterns of cacined mesoporous silica synthesized with \( C_n \)AS and TMAPS, where \( n = 12, 14, 16 \) and 18. The synthesis conditions are: TMAPS/\( C_n \)AS = 1, TEOS/\( C_n \)AS = 8, the concentration of surfactant in water is 1 wt%.

Table 9. Mesostructure and porous properties of the calcined AMS mesoporous silicas synthesized with \( C_n \)AS of different chain lengths as the template and TMAPS as the CSDA.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Mesostructure</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{12} )AS</td>
<td>3d-cubic</td>
<td>269</td>
<td>0.22</td>
<td>3.2</td>
</tr>
<tr>
<td>( C_{14} )AS</td>
<td>2d-hexagonal ( p6mm )</td>
<td>520</td>
<td>0.53</td>
<td>3.7</td>
</tr>
<tr>
<td>( C_{16} )AS</td>
<td>2d-hexagonal ( p6mm )</td>
<td>387</td>
<td>0.51</td>
<td>5.2</td>
</tr>
<tr>
<td>( C_{18} )AS</td>
<td>Lamellar</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.4.3 Effect of the geometry of the CSDA

Figure 37. XRD patterns of the calcined mesoporous silicas synthesized with $\text{C}_{14}\text{GluA}$ and different types of CSDA: (a) APS, (b) MAPS and (c) DMAPS. The chemical compositions are: (I) $\text{C}_{14}\text{GluA}$: CSDA: TEOS: $\text{H}_2\text{O}$: HCl = 1: 2: 15: 2000: 1.0.

In the formation of AMS, the CSDA interacts with the headgroups of the anionic surfactant electrostatically. The amino groups or quaternary ammonium groups of the CSDA act as the counterions of the headgroups of the anionic surfactant. Therefore, the geometry of the CSDA affects the mesophase by affecting the effective headgroup areas of the surfactants by the means of the steric effect. A larger CSDA in geometry gives rise to larger effective headgroup area of surfactant in micelles and thus lower organic/inorganic interface curvature of the resultant mesoporous silica.

Figure 37 shows the XRD patterns of mesoporous silicas prepared with APS, MAPS and DMAPS having an increasing geometry as the CSDA. It can be seen that the mesostructure differs with the types of CSDA. The mesostructure synthesized with APS as the CSDA is typically 2d-hexagonal $p6mm$. The mesostructure synthesized with MAPS is a mixture of 2d-hexagonal $p6mm$ and bicontinuous cubic $Pn-3m$, which can be revealed by the TEM images (Figure 38) and its XRD pattern. The mesostructure synthesized with DMAPS which has the largest geometry is typically bicontinuous cubic $Pn-3m$. 
Therefore, it can be concluded that, the geometry of CSDA can affect the mesostructure by the steric effect. Larger CSDA in geometry leads to lower organic/inorganic interface curvature of the mesostructure.

![Figure 38](image)

*Figure 38.* HRTEM images of the calcined mesoporous silicas with XRD patterns shown in Figure 37b. The images were taken with electron beams perpendicular to the cylindrical pores of 2d-hexagonal structure (a) and along [211] zone axis of bicontinuous cubic $Pn-3m$ structure (b).

### 4.4.4 A rational synthesis of thick-walled mesoporous silica

Mesoporous silica with high hydrothermal stability has been a long pursuit which could find enormous application in industry. One solution is to create mesoporous silica with thick wall, which is thought to enhance the stability of the materials. However, the control of wall thickness of mesoporous materials is still a challenge.

In this work we synthesized a thick-walled mesoporous silica material by the molecular design route. A fatty alcohol ether carboxylate (AEC) surfactant was used as the template (Figure 39), and co-structure-directing method was used to synthesize mesoporous silica, using APS or TMAPS as the CSDA.

![Figure 39](image)

*Figure 39.* Structure of AEC surfactant.

The AEC surfactant has three parts, including alkyl group, poly(ethyl oxide) (PEO) and carboxylate. It can be regarded as a nonionic surfactant with a carboxylate modification, or an anionic surfactant with PEO inserted into the molecule. Therefore, this kind of surfactant has the properties of both a nonionic surfactant and an anionic surfactant. In the organic/inorganic self-assembly in forming mesoporous silicas, PEO interacts with siliceous oligomers by hydrogen bonding ($S^\text{H}H^\text{T}$), and carboxylate interacts with CSDA by electrostatic interactions. These two types of interactions between AEC surfactant and inorganic species give rise to two types of silica walls of mesoporous silica. Therefore, the material obtained has a double-layer silica...
wall structurally, and consequently its wall thickness is dramatically enlarged.

![Figure 40. XRD patterns of calcined mesoporous silicas synthesized with C_{12}H_{25}O(CH_{2}CH_{2}O)_{10} OH (a), C_{13}H_{27}COONa (b) and C_{12}H_{25}O(CH_{2}CH_{2}O)_{10}CH_{2}COONa (c).](image)

![Figure 41. HRTEM images of calcined mesoporous silicas synthesized with C_{12}H_{25}O(CH_{2}CH_{2}O)_{10} OH (a), C_{13}H_{27}COONa (b) and C_{12}H_{25}O(CH_{2}CH_{2}O)_{10}CH_{2}COONa (c).](image)

Figure 40 shows the XRD patterns of mesoporous silicas prepared with nonionic, anionic and AEC surfactants as the template. Their TEM images are shown in Figure 41. For the purpose of comparison, the alkyl chain length has been fixed, and the lengths of PEO part of nonionic and AEC surfactants are kept the same. All the samples have ordered 2d-hexagonal \( p6mm \) structures, which can be derived from the XRD pattern and confirmed by the TEM images.

Among these materials, AEC templated mesoporous silica has the largest unit cell parameter, which can be inferred from the XRD patterns and TEM images. The pore sizes of the materials are almost the same, which can be revealed by nitrogen adsorption data, due to the same length of porogen (al-
kyl chain). The structural and porous properties of the mesoporous silicas are shown in Table 10, in combination of XRD and nitrogen adsorption results.

Table 10. Structural properties of calcined mesoporous silicas synthesized with different types of surfactants.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>(a) (nm)</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>(V_p) (mm(^3) g(^{-1}))</th>
<th>(d) (nm)</th>
<th>(w) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O(CH}_2\text{CH}<em>2\text{O})</em>{10}\text{OH})</td>
<td>5.4</td>
<td>814</td>
<td>840</td>
<td>3.4</td>
<td>2.0</td>
</tr>
<tr>
<td>(\text{C}<em>{13}\text{H}</em>{27}\text{COONa})</td>
<td>6.4</td>
<td>542</td>
<td>590</td>
<td>3.6</td>
<td>2.8</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O(CH}_2\text{CH}<em>2\text{O})</em>{10}\text{CH}_2\text{COONa})</td>
<td>7.2</td>
<td>472</td>
<td>520</td>
<td>3.8</td>
<td>3.4</td>
</tr>
</tbody>
</table>

\(^a\) Notation: \(a\), unit cell parameter; \(S_{\text{BET}}\), BET specific surface area; \(V_p\), mesopore volume; \(d\), BJH pore diameter calculated on the basis of N\(_2\) desorption isotherm curves; \(w\), wall thickness.

From Table 10 it can be seen that the AEC templated mesoporous silica have the largest unit cell parameter (\(a = 7.2\) nm) and wall thickness (\(w = 3.4\) nm) among these three kinds of materials, which is as expected from the perspective of molecular design and justifies our strategy.

Figure 42. XRD patterns of the mesoporous silicas obtained by refluxing the calcined samples in boiling water for 24 h. The materials were templated by \(\text{C}_{12}\text{H}_{25}\text{O(CH}_2\text{CH}_2\text{O})_{10}\text{OH}\) (a), \(\text{C}_{13}\text{H}_{27}\text{COONa}\) (b) and \(\text{C}_{12}\text{H}_{25}\text{O(CH}_2\text{CH}_2\text{O})_{10}\text{CH}_2\text{COONa}\) (c), respectively.

The hydrothermal stability of the three kinds of mesoporous materials using different types of surfactants as the template was further investigated. The materials were treated with boiling water and refluxed for 24 hours, and the XRD patterns of the materials were then taken, as shown in Figure 42. It can be seen that the XRD patterns of mesoporous silicas synthesized with
nonionic and anionic surfactants as the CSDA shows no reflection peaks, indicating a complete collapse of the mesostructure after hydrothermal treatment. However, a significant strong X-ray reflection peak remains for the AEC templated mesoporous silica after treatment, which strongly indicates its high hydrothermal stability.

The wall thickness of AEC templated mesoporous silica could be well tuned by changing the average length of PEO part. As table 11 shows, the silica wall is thickened from 2.8 nm to 3.4 nm gradually, when the number of EO unit increases from 5 to 10 step by step, suggesting its high designability.

Table 11. Structural properties of calcined mesoporous silicas synthesized by AEC with different length of (EO)x-block.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>(a) (nm)</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>(V_p) (mm(^3) g(^{-1}))</th>
<th>(d) (nm)</th>
<th>(w) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_2\text{COONa}))</td>
<td>6.5</td>
<td>664</td>
<td>760</td>
<td>3.7</td>
<td>2.8</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_2\text{COONa}))</td>
<td>6.6</td>
<td>473</td>
<td>590</td>
<td>3.7</td>
<td>2.9</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_2\text{COONa}))</td>
<td>6.8</td>
<td>518</td>
<td>690</td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_8\text{CH}_2\text{COONa}))</td>
<td>7.0</td>
<td>558</td>
<td>720</td>
<td>3.8</td>
<td>3.2</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}((\text{CH}_2\text{CH}_2\text{O})_9\text{CH}_2\text{COONa}))</td>
<td>7.1</td>
<td>528</td>
<td>660</td>
<td>3.8</td>
<td>3.3</td>
</tr>
<tr>
<td>(\text{C}<em>{12}\text{H}</em>{25}\text{O}((\text{CH}_2\text{CH}<em>2\text{O})</em>{10}\text{CH}_2\text{COONa}))</td>
<td>7.2</td>
<td>472</td>
<td>520</td>
<td>3.8</td>
<td>3.4</td>
</tr>
</tbody>
</table>

\(a\) Notation: \(a\), unit cell parameter; \(S_{\text{BET}}\), BET specific surface area; \(V_p\), mesopore volume; \(d\), BJH pore diameter calculated on the basis of N\(_2\) desorption isotherm curves; \(w\), wall thickness.

4.5 Pore size control of AMS materials

4.5.1 Pore size control by alkyl length of surfactant

The pore size of AMS is highly dependent on the hydrophobic alkyl chain length, which is similar to the mesoporous silicas synthesized by cationic or nonionic surfactants, because the size of micelles are proportional to the alkyl length of surfactant.

The effect of alkyl chain length on the pore size has been demonstrated in Table 9. The longer alkyl chain of fatty acid has proved to give rise to larger mesopores of silica materials.
4.5.2 Pore size change with ionization degree of surfactant

It has been demonstrated that the mesostructure of AMS is highly affected by the ionization degree of surfactant. Nitrogen adsorption data shows that, the pore size of the mesoporous silica differs significantly at different ionization degree of surfactant.

For a typical instance, mesoporous silicas GluA-TM-NaOH-\(x\) (\(x\), NaOH/\(C_{14}\)GluA) were synthesized by using \(C_{14}\)GluA and TMAPS with addition of different amount of NaOH. The nitrogen adsorption/desorption isotherms and pore size distributions of the calcined samples are displayed in Figure 43, and the porous properties are summarized in Table 12.

![Figure 43](image)

**Figure 43.** Nitrogen adsorption isotherms and pore size distributions of the calcined mesoporous silica GluA-TM-NaOH-\(x\), where \(x\) = (a) 2.0, (b) 1.5, (c) 1.0, and (d) 0.75. The isotherms a-c are offset vertically by 50, 100 and 100 cm\(^3\)/g STP respectively.

**Table 12.** Porous properties of mesoporous silicas synthesized with \(C_{14}\)GluA and TMAPS, GluA-TM-NaOH-\(x\).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mesostructure (space group)</th>
<th>Pore type</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore Volume (cm(^3)/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GluA-TM-NaOH-2.0</td>
<td>Tetragonal (P4 ( \bar{2} )/ ( mmn ))</td>
<td>Cage type</td>
<td>535</td>
<td>0.275</td>
<td>2.2</td>
</tr>
<tr>
<td>GluA-TM-NaOH-1.5</td>
<td>Cubic ((Fd\bar{3}m))</td>
<td>Cage type</td>
<td>421</td>
<td>0.262</td>
<td>2.8</td>
</tr>
<tr>
<td>GluA-TM-NaOH-1.0</td>
<td>2d-hexagonal ((p6mm))</td>
<td>Cylindrical</td>
<td>495</td>
<td>0.510</td>
<td>3.5</td>
</tr>
<tr>
<td>GluA-TM-NaOH-0.75</td>
<td>Cubic ((Pn\bar{3}m))</td>
<td>Cylindrical</td>
<td>493</td>
<td>0.650</td>
<td>4.7</td>
</tr>
</tbody>
</table>
It can be inferred that the mesoporous silica materials have typical type IV isotherms and high porosity with unique pore sizes. As the ionization degree of the surfactant C_{14}GluA becomes lower (\( \alpha \) changes from 2.0 to 0.75), the pore size shifts gradually to a larger value from 2.2 nm to 2.7 nm, accompanied by a decrease in organic/inorganic interface curvature of the mesostructure.

In addition, when using C_{14}GluA of different ionization degree as the template and APS as the CSDA, the obtained mesoporous silica materials have different mesostructures ranging from cage-type to bicontinuous, and the pore size changes from 2.4 nm to 4.2 nm, accordingly, as the sorption data shown in Table 13 indicate. Therefore, it can be inferred that the pore size change is related to the ionization degree of surfactant and the mesostructure change, and is independent on the type of CSDA.

Table 13. Porous Properties of mesoporous silicas synthesized with C_{14}GluA and APS, GluA-AP-HCl-\( \alpha \).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mesostructure (space group)</th>
<th>Pore type</th>
<th>Surface area (( \text{m}^{2}\text{g}^{-1} ))</th>
<th>Pore Volume (( \text{cm}^{3}\text{g}^{-1} ))</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GluA-AP-HCl-0</td>
<td>Modulated mesostructure</td>
<td>Cage type</td>
<td>540</td>
<td>0.30</td>
<td>2.4</td>
</tr>
<tr>
<td>GluA-AP-HCl-1.6</td>
<td>Cubic (\text{Fd}\text{3m})</td>
<td>Cage type</td>
<td>616</td>
<td>0.48</td>
<td>2.9</td>
</tr>
<tr>
<td>GluA-AP-HCl-2.4</td>
<td>2d-hexagonal (\text{p}6\text{mm})</td>
<td>Cylindrical</td>
<td>813</td>
<td>0.68</td>
<td>3.1</td>
</tr>
<tr>
<td>GluA-AP-HCl-2.8</td>
<td>2d-hexagonal (\text{p}6\text{mm})</td>
<td>Cylindrical</td>
<td>805</td>
<td>0.89</td>
<td>3.9</td>
</tr>
<tr>
<td>GluA-AP-HCl-3.0</td>
<td>Cubic (\text{Pn}\text{3m})</td>
<td>Cylindrical</td>
<td>673</td>
<td>0.81</td>
<td>4.2</td>
</tr>
</tbody>
</table>

It is known that the length of an alkyl chain in crystalline state is calculated as \( l(\text{crystal}) = 1.5+1.26n \) (Tanford's formula), where \( n \) represents the number of carbon atoms, and the chain length in molten phase is about 80% of this value. Therefore, the chain length of molten C_{14}GluA is roughly 2 nm. When forming micelles to form the above mesostructures, the diameter of the micelle should be twice of the value, that is, around 4 nm, which is close to the pore size of low curvature mesophases (bicontinuous \( \text{Pn-3m} \)), much larger than the pore size of high curvature mesophases (\( \text{P4}_2/\text{mmn, Fd-3m, etc} \)).

Based on these calculations, a schematic mechanism could be derived for the change of pore size during the change of ionization degree of surfactant and mesostructure, as shown in Figure 44. At a low ionization of anionic surfactant, the headgroups are closely packed, while at a high ionization of surfactant, the headgroups are apart from each other. In the latter case, the hydrophobic “tail” of the surfactant, rather than self-assembling loosely
which is thermodynamically unfavorable, would coil” to fill the space and thus maximize their van der Waals hydrophobic forces, leading to lowering of the overall energy and consequently smaller pore size. Therefore, the driving force of the pore size change is thermodynamics.

![Figure 44. Illustration of the pore size change with mesophase curvature. Larger surface curvature with larger head group area (a) leads to more windings of the surfactant tails due to the van der Waals forces, which results in a smaller pore size and d-spacings, while smaller surface curvature leads to an enlarged pore size (b).]

It is noteworthy that the pore size change with ionization degree of surfactant is not prominent for monoprotic surfactants templating systems, e.g. C\textsubscript{14}AS, C\textsubscript{16}ValS, etc. It is coincide with our proposal shown in Figure 44, because for monoprotic surfactants the density of alkyl chains in a micelle is high for most systems, which eliminates the contraction effect of pore size caused by thermodynamics. And in this case, the pore size of the resultant mesoporous silica is more dependent on the length of the alkyl chain of the surfactant, which is close to the value approximated by the Tanford's formula.

### 4.5.3 Pore size control by CSDA/surfactant ratio

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mesostructure</th>
<th>Surface area (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>Pore Volume (cm\textsuperscript{3}g\textsuperscript{-1})</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS/C\textsubscript{18}GluA = 2</td>
<td>Disordered</td>
<td>532</td>
<td>0.71</td>
<td>4.1</td>
</tr>
<tr>
<td>APS/C\textsubscript{18}GluA = 4</td>
<td>Disordered</td>
<td>687</td>
<td>0.61</td>
<td>3.5</td>
</tr>
<tr>
<td>APS/C\textsubscript{18}GluA = 6</td>
<td>3d-cubic Fm\textsubscript{3}m</td>
<td>603</td>
<td>0.43</td>
<td>2.9</td>
</tr>
<tr>
<td>APS/C\textsubscript{18}GluA = 8</td>
<td>3d-cubic Fm\textsubscript{3}m</td>
<td>598</td>
<td>0.32</td>
<td>2.3</td>
</tr>
</tbody>
</table>
The pore size of AMS is also affected by the CSDA/surfactant ratio. Table 14 shows a summary of porous properties of calcined mesoporous silicas using C\textsubscript{18}GluA as the template and different amount of APS as the CSDA.

It is clearly shown that, when the APS/C\textsubscript{18}GluA rises from 2 to 8, the pore size changes accordingly from 4.1 nm to 2.3, which is decreasing dramatically. It is worth noting that the mesostructure changes from a disordered cage-type mesophase (judged from TEM and nitrogen, not shown) to cage-type $Fm-3m$ mesophase in this process.

The change of the size of the mesopores with the APS/C\textsubscript{18}GluA ratio can be attributed to the interactions between the pendant organic groups on the silica wall and the micelles. Aminopropyl groups are hydrophobic in nature, which could interact with the hydrophobic core of micelles by hydrophobic force. This hydrophobic interaction has the capability to drive the wall to the core of the micelle. As the scheme in Figure 45 shows, the higher the loading of the aminopropyl groups on the pore walls, then the stronger the interaction is and the smaller the pore size will be. This effect has been discovered before by Pinnavaia \textit{et al} and Ozin \textit{et al} when functionalizing MCM-41 with different organic groups, \cite{130,131} which is fairly consistence with our results.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure45.png}
\caption{Scheme for the interactions between the electrostatically neutral APS and the hydrophobic core of the micelles which lead to different pore sizes.}
\end{figure}

It is worth noting that the hydrophobic force between pendant CSDA on the silica wall and the hydrophobic core of micelles exists especially in AMS systems using aminosilane as the CSDA, \textit{e.g.} APS, MAPS and DMAPS, because of the hydrophobicity of these groups. TMAPS, on the other hand, is ionized and hydrophilic, and thus the discussion is not applicable for this system.
5 Conclusions

This dissertation has been focused on the synthesis, characterization and formation mechanisms of anionic-surfactant-templated mesoporous silica (AMS).

(1) Ionization degree of anionic surfactant controls the organic/inorganic interface curvatures of mesoporous silica.

Mesophases with different organic/inorganic interface curvatures, varying from cage type (tetragonal $P4_{2}/mmn$; cubic $Pm-3n$ with modulations; cubic $Fd-3m$) to cylindrical (2d hexagonal $p6mm$), bicontinuous (cubic $Ia-3d$ and $Pn-3m$), and lamellar, have been obtained by using diprotic or monoprotic anionic surfactant as the template and APS or TMAPS as the CSDA, by the means of controlling the acidity or alkalinity of reaction systems.

It has been proposed that in this process the acidity or alkalinity affects the ionization degree of anionic surfactant, which dominates the change of mesophases. Equilibrium is reached between the electrostatic neutral and the negatively charged surfactant molecules in solution. When the alkalinity of the synthesis system is low, the ionization equilibrium of anionic surfactant favors the formation of neutral species, which makes a low charge density of the micelles and therefore low electrostatic repulsions between surfactant headgroups. As a result, the effective surfactant headgroup area is small, which gives a large surfactant packing parameter, $g$, according to its definition $g = V/a_0 h$. Consequently, the silica mesoporous structure has a low hydrophilic/hydrophobic or organic/inorganic interface curvature. When the alkalinity of the synthesis system of AMS rises, on the other hand, anionic surfactants become more ionized, which leads to an increase in the repulsive electrostatic forces between headgroups of surfactants and thus high organic/inorganic interface curvature of the resultant mesophase.

(2) Mesocage/mesocage electrostatic repulsive interactions affect their packing manner and determine the cage-type mesostructure.

The synthesis system for mesophase formation using diprotic $C_{14}$GluA as the template and TMAPS as the CSDA has been investigated and a full-scaled synthesis-field diagram has been shown. In this diagram cage-type phases including cubic $Fm-3m$, $Pm-3n$, $Fd-3m$, tetragonal $P4_{2}/mmn$ have been obtained by varying the $C_{14}$GluA/NaOH/TMAPS composition ratios.
It has been concluded that the formation of cage-type mesophase is affected by the mesocage/mesocage electrostatic interaction. The charging of a mesocage determines its softness. A mesocage with high charging density can be regarded as a “hard sphere”, the packing of which is determined by close packing, leading to formation of \( \text{Fm-3m, etc.} \) When the mesocages have low charge density, they can be regarded as “soft spheres”, the packing of which is determined by a compromise between close packing and minimization of surface area. In this case, \( \text{Fd-3m, Pm-3n} \) and \( \text{P4}_2/\text{mmm} \) are favored. In the “soft sphere” packing, the electrostatic repulsive interaction between mesocages determines their packing manner. When the interaction between mesocages is weak, \( \text{Fd-3m} \) and \( \text{Pm-3n} \) are favored to form; while when the interaction becomes strong, \( \text{P4}_2/\text{mmm} \) is more favored.

(3) Molecular characteristics can be reflected in the structural properties of AMS materials.

The formation of AMS has been investigated on the basis of the design of structure and geometry of the anionic surfactant and the CSDA. Anionic surfactants with larger area head groups or shorter length alkyl chains favored the formation of mesoporous silicas with larger organic/inorganic interface curvatures. The geometry of the CSDA, which interacts with anionic surfactant and is located in the hydrophilic part of the micelles, also affected the resultant mesophase by the means of a steric effect. Larger CSDAs favored the formation of mesophases with larger organic/inorganic interface curvature. Therefore, the structural properties of AMS materials can be tuned by the molecular design route.

Based on this strategy, a thick-walled mesoporous silica material was achieved. A fatty alcohol ether carboxylate (AEC) surfactant was used as the template and co-structure-directing method was used to synthesize mesoporous silica. In the organic/inorganic self-assembly in forming mesoporous silicas, PEO part of AEC surfactant interacts with siliceous oligomers by hydrogen bonding (\( \text{S}^\text{OH}+\text{I}^- \)), and carboxylate interacts with CSDA by electrostatic interactions. These two types of interactions between AEC surfactant and inorganic species give rise to two types of silica walls of mesoporous silica and thus thick silica wall. The hydrothermal stability of the mesoporous silica proved to be highly enhanced.

(4) The pore size of AMS is controlled by alkyl length and ionization degree of surfactant and the CSDA/surfactant ratio.

The alkyl chain length determines the size of the micelle, which is the porogen of silica materials. Therefore, the longer alkyl chain of surfactant leads to larger size of mesopores.

Larger ionization degree of a diprotic anionic surfactant gives rise to small pore sizes, the driving force of which has been considered as thermodynamics. At a low ionization degree of anionic surfactant, the headgroups
are closely packed, while at a high ionization degree of surfactant, the headgroups are apart from each other. In the latter case, the hydrophobic “tail” of the surfactant, rather than self-assembling loosely which is thermodynamically unfavorable, would coil” to fill the space and thus maximize their hydrophobic forces, leading to lowering of the overall energy and consequently a contraction of pore size.

The ratio of CSDA/surfactant affects the pore size of AMS, especially for the aminosilane types of CSDA. This effect has been attributed to the hydrophobic interactions between the pendant organic groups on the silica wall and the hydrophobic core of the micelles, which would drive the wall to the core of the micelle. The higher the loading of the aminopropyl groups on the pore walls, the stronger the hydrophobic interaction is and thus the smaller the pore size will be.

(5) A novel bicontinuous cubic \( Pn\)-3m mesoporous structure was prepared with a diprotic anionic surfactant and characterized by electron crystallography and inverse replication.

A novel bicontinuous cubic \( Pn\)-3m mesoporous structure (AMS-10) was prepared using diprotic glutamic acid derived anionic surfactant as the template by using the versatile co-structure-directing synthesis route.

A 3d-reconstruction of the structure of AMS-10 was conducted by electron crystallography. It has been derived that AMS-10 (\( Pn\)-3m) has a bicontinuous structure composed of an enantiomeric pair of 3d mesoporous networks that are interwoven with each other. Each network, which is divided by a D (diamond) surface, consists of tetrahedral connection of mesopores.

Indirect characterization, inverse replication, was employed to reveal further structural information of AMS-10. A replication of two sets and one set of bicontinuous mesochannels were achieved by \( \text{Co}_3\text{O}_4 \). A possibility can be derived that ordered complimentary micropores might exist in the thinnest parts of the silica wall of \( Pn\)-3m bicontinuous structure, which leads to the diffuse of guest precursors within different sets of mesochannels and replication of two sets of the bicontinuous mesopores.
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7 References


