The synthesis of hollow silica nanostructures by co-assembly of silica and surfactants

Yao, Lin

2014

Yao, L. (2014). The synthesis of hollow silica nanostructures by co-assembly of silica and surfactants. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/60763>

<https://doi.org/10.32657/10356/60763>

The Synthesis of Hollow Silica Nanostructures by Co-assembly of Silica and Surfactants

YAO Lin

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy

Singapore

May 2014

Advisor: Associate Professor Chen Hongyu

Acknowledgement

During the past several years, there are so many people who give kindly helps and support to me in my graduate study. I want to thank all of them very much.

At first, I would like to express my sincerest gratitude to my advisor, Prof. Chen Hongyu. Thanks for his wonderful training in mechanism study and for his patience and guidance.

It is my great pleasure to study and work together with all group members. Thank Feng Yuhua, Chen Liyong, Shen Xiaoshuang, Sun Hang, Zhu Liangfang, Chen Gang, Chen Tao, Wang Hong, Liu Cuicui, He Jiating, Xu Jun, Wang Yawen, Sindoro Melinda, Tan Lee Siew Rachel, for the kindly helps and suggestions when I started my research in the lab. Thank Chong Wen Han for your patient help of the SEM characterization. Thank Song Xiaohui, Wang Jiangyan, Su Dongmeng, Mikhail Moiseev, Pan Ming, Ding Tao and Wang Weizhi for your helpful discussions. Thank other former group members for your help.

At last, I would like to give my warm thanks to my family, especially my wife, for the totally support and understanding in these years.

Contents

Acknowledgement	III
Abbreviations	VII
Abstract	VIII
Chapter 1 Introduction	1
1.1 Nanotechnology	1
1.2 Nanostructure and silica nanostructure	1
1.3 Silica nanoparticle	5
1.4 Silica core-shell structures	6
1.5 Hollow silica nanostructure	9
1.6 Mesoporous silica nanoparticle	15
1.7 Helical mesoporous silica nanostructure	17
1.8 Silica vesicle	21
1.9 Bibliography	21
Chapter 2 Bilayer Silica Vesicles: Understanding the Cylinder-to-Vesicle Phase Transition of Mesoporous Silica	35
2.1 Introduction	35
2.2 Materials and Methods	38
2.2.1 Materials	38
2.2.2 Methods	38
2.3 Results and Discussions	40
2.3.1 Phase diagram summarizing the cylinder-to-vesicle transition of mesoporous silica	40
2.3.2 Delayed addition of MPTMS	52
2.3.3 Trapping the intermediates before the formation of MCM-41 phase or silica vesicle	61
2.4 Conclusion	64
2.5 Bibliography	65
Chapter 3 Application: Encapsulation of Hydrophobic Fluorescent Dyes and Formation of Core-shell Nanostructures with Mesoporous Silica Shells	68

3.1 Introduction.....	68
3.2 Materials and Methods	70
3.2.1 Materials.....	70
3.2.2 Methods.....	71
3.3 Results and Discussions	74
3.3.1 Synthesis of Double Layer Silica Vesicles and Drug Loading	74
3.3.2 Study the release process of hydrophobic dyes loaded in silica vesicles.....	80
3.3.3 Synthesis of core-shell nanostructures with mesoporous silica shells.	81
3.3.4 Synthesis the chain of Fe ₃ O ₄ @mesoporous silica nanostructures.....	86
3.3.5 Synthesis of new silica nanoparticles with ordered nanochannels by doping stearic acid molecule with CTAB	90
3.4 Conclusion.....	93
3.5 Bibliography	94
Chapter 4 Understanding and Application of Dissolution Re-growth Process during Silica Vesicles Formation	98
4.1 Introduction.....	98
4.2 Materials and Methods	100
4.2.1 Materials.....	100
4.2.2 Methods.....	101
4.3 Results and Discussions	105
4.3.1 Synthesis of double layer silica vesicles and reaction with additional amount of CTAB to explore the dissolution re-growth process	105
4.3.2 Doping of copper-ammonia complex into silica vesicles.	111
4.3.3 Doping of aluminum into silica vesicles to form aluminosilica nanostructures and loading Rhodamine B base into aluminosilica vesicles.	113
4.3.4 Modify the formation of silica vesicles and doping of gold nanoparticles into silica vesicles to apply in the reduction reaction.	116
4.4 Conclusion.....	122
4.5 Bibliography	123
Chapter 5 Explore the Formation Process of Helical Mesoporous Silica.....	127

5.1 Introduction.....	127
5.2 Materials and Methods	129
5.2.1 Materials.....	129
5.2.2 Methods.....	130
5.3 Results and Discussions.....	133
5.3.1 Synthesis of primary helical MCM-41 mesoporous silica and encapsulated by second layer of silica shell.	133
5.3.2 Explore the formation of helical mesoporous silica by doping metal species.	138
5.3.3 To explore the formation of helical mesoporous silica by adding acid or additional amount of CTAB.....	142
5.3.4 Explore the formation of helical mesoporous silica by doping organic molecules.	145
5.3.5 Characterization of large diameter helical mesoporous silica.....	152
5.4 Conclusion.....	156
5.5 Bibliography	157
Chapter 6 General Study of Core-Shell silica nanostructures	160
6.1 Introduction.....	160
6.2 Materials and Methods	161
6.2.1 Materials.....	161
6.2.2 Methods.....	162
6.3 Results and Discussions	166
6.3.1 The stability of silica in SiO ₂ NPs and core-shell silica NPs.....	166
6.3.2 Doping of Cationic Species in Silica NPs.....	173
6.3.3 Doping of Cationic Species in AuNPs@SiO ₂ nanoparticles.....	177
6.3.4 Doping of Cationic Species in Fe ₃ O ₄ NPs@SiO ₂ nanoparticles. .	189
6.4 Conclusion.....	191
6.5 Bibliography	191
Chapter 7 Summary and Outlook	195
7.1 Summary.....	195
7.2 Outlook	200
List of Publications	203

Abbreviations

CTAB	Hexadecyl trimethylammonium bromide
TMB	1, 3, 5-trimethylbenzene
TEOS	Tetraethoxysilane
MPTMS	(3-Mercaptopropyl)trimethoxysilane
APTMS	(3-Aminopropyl)trimethoxysilane
APTES	(3-Aminopropyl)triethoxysilane
AAPTMS	[3-(2-aminoethylamino)propyl]trimethoxysilane
NPs	Nanoparticles
AuNPs@SiO ₂	Silica encapsulated Au nanoparticles
Fe ₃ O ₄ @SiO ₂	Silica encapsulated Fe ₃ O ₄ nanoparticles
HRP	Horseradish peroxidase
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
UV-vis	Ultraviolet-visible spectroscopy

Abstract

My postgraduate research focused on the synthesis of hollow silica nanostructures by co-assembly of silica and surfactants. It is summarized in the thesis. The major projects include understanding the cylinder-to-vesicle phase transition of mesoporous silica, the application in encapsulation of hydrophobic dyes in silica vesicles and fabrication of core-shell nanostructures with mesoporous silica shells, exploration and application of the dissolution and re-growth process in the formation of silica nanostructures, studying the formation of helical mesoporous silica, and researching on the stability of silica and doping cationic species into silica nanostructures.

In chapter 2, we study the cylinder-to-vesicle phase transition of mesoporous silica and the inter-dependence of the controlling factors. As summarized in a phase diagram, the outcome of the surfactant-silica co-assembly can be rationally controlled just like soft micelles, which depends on the concerted effects of the ingredients. The trends can be explained using packing parameters. By trapping intermediates and studying how the hardening silica affects molecular diffusion, this new system provides windows for inferring the complex interactions among the ingredients, which are hard to study by conventional methods. The cylinder-to-vesicle transition reveals basic

principles underlying the phase control. Such understanding permits insights in the unique behaviors of surfactant-silica co-assembly and grants readily control of the phases of mesoporous silica.

In chapter 3, we have developed a new method to dope hydrophobic dyes into silica nanostructures by using 1, 3, 5-trimethylbenzene (TMB) solution dissolved with hydrophobic dyes instead of pure TMB in the formation of silica vesicles. The hydrophobic dyes can be trapped successfully without change the morphology of silica vesicles. We also studied the slowly release process of perylene molecules from silica nanostructures to empty CTAB micelle solution. On the other hand, we have proved the clumps to evolve into ordered MCM-41 to synthesize metal silica nanostructures by understanding the inter-dependence of (3-mercaptopropyl)trimethoxysilane (MPTMS) and TMB in controlling the phase outcome. In addition, new silica nanoparticles with ordered channels were found by doping stearic acid molecules with CTAB in the formation of initial clumps.

In chapter 4, we have explored the process of silica dissolution and re-growth in the formation of silica vesicle by trapping the intermediates. The similar results were observed by using half amount of CTAB compared to the synthesis of silica vesicles. Based on the existence of silica dissolution and re-growth in the silica vesicle formation, we doped functional molecules into the silica vesicles to synthesize new functional silica nanostructures. On the other hand,

we also modified the formation of silica vesicles by using APTMS or AAPTMS instead of MPTMS to get new silica nanostructures. In the case of using APTMS to initiate the formation of silica vesicle, HAuCl_4 molecule was doped into the silica nanoparticles and reduced by NaBH_4 to get small size Au nanoparticles doped with hollow silica nanostructures. After that, we tested the catalytic activity of Au NPs doped hollow silica nanostructures in the reduction reaction of 4-nitrophenol converted to 4-aminophenol.

In chapter 5, we study the formation mechanism of helical mesoporous silica. According to Qiao group's method, we prepared helical mesoporous silica by using MPTMS and TEOS as silica source with CTAB as template. To study the formation mechanism of helical mesoporous silica, we try to modify the formation process of helical mesoporous silica with different approach. Firstly, we encapsulated the helical mesoporous silica with the second layer of silica. Secondly, we doped functional molecule to get different silica nanostructure. Finally, we synthesized large size of mesoporous silica rod by using helical mesoporous silica as seed. We also synthesized large size silica nanostructure from helical mesoporous silica as seed by using APTES instead of MPTMS.

In chapter 6, we have explored the stability of silica shell in silica nanoparticles and AuNPs@SiO_2 nanoparticles. The stability of silica NPs has relationship with the species of cationic ions. In the synthesis of AuNPs@SiO_2 nanoparticles by Stöber method, the more amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ was used, the

silica shell was harder to be etched. When the AuNPs@SiO₂ nanoparticles was synthesized by using NaOH as catalyst and incubated in CuCl₂ or FeCl₃, the silica shell was very hard to be etched in hot water. In addition, the HCl and HNO₃ molecule can also hard the silica shell. But the silica shell became easy to be etched in hot water by incubating in CaCl₂ or BaCl₂. On the other hand, we successfully doped functional molecule into silica nanostructures using the Stöber method. The cationic species were doped between the two layers of silica shells in the silica nanostructures.

Chapter 1 Introduction

1.1 Nanotechnology

Nanotechnology is the manipulation of matter on an atomic and molecular scale. National Nanotechnology Initiative from USA defines nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100nm. It is very broad, including fields of science such as surface science, organic chemistry, molecular biology, semiconductor physics, and microfabrication.^[1] The research and applications are ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale. It is potential to create many new materials and devices with a vast range of application, such as in medicine, electronics, biomaterials and energy production. The current research of nanotechnology includes bottom-up approaches,^[2] top-down approaches, functional approaches,^[3] biomimetic approaches,^[4] and speculative.^[5-6]

1.2 Nanostructure and silica nanostructure

A nanostructure is an object of intermediate size between microscopic and molecular structures. According to the number of dimensions on the nanoscale, there are three basic types of nanostructures: firstly, it only has one dimension

on the nanoscale, for example, only the thickness of the surface of nanotextures is between 0.1 and 100 nm. Secondly, it has two dimensions on the nanoscale, for example, the diameter of the nanotube is between 0.1 and 100 nm but its length could be much greater. Thirdly, there are three dimensions on the nanoscale, for example, spherical nanoparticle is between 0.1 and 100 nm in each spatial dimension. The list of nanostructures includes nanocages,^[7-9] nanofibers,^[10-11] nanoflowers,^[12-13] nanomeshes,^[14-16] nanoparticles,^[17-27] nanorings,^[28-31] nanorods,^[32-35] nanoshells,^[36-38] nanocomposite,^[39-41] and so on.

Our group demonstrated a unique capability in partially oxidizing the polyaniline shell on gold nanoparticles to polyaniline. Because of the solubility difference, the unreacted inner shell section can be selectively dissolved by 2-propanol, giving yolk-shell nanostructures and, thus, making it possible for assessing the oxidized section (Figure 1-1).^[25]

Our group also showed that bundles of carbon nanotubes can be coiled into ring structures by controlling the contraction of their polymer shells. With the robust carbon nanotubes, we demonstrated their reversible transformation between circular and compressed rings in a colloid (Figure 1-2).^[30]

Figure 1-1 (a) Schematics illustrating the fabrication of Au@PANI yolk-shell NPs. TEM images of (b, c) Au@OANI core-shell NPs at low and high magnification, respectively. (d) IR spectra of (1) Au@OANI and (2) Au@PANI NPs (asterisks indicate peaks of interest). (e, f) After treating sample (b) with HAuCl_4 for 6 h, imaged at low and high magnification, respectively; and (g) after etching sample (e) with 2-propanol for 2 h. The arrow indicates a hollow PANI shell formed in the absence of Au core. Reprinted with permission from ref 25, respectively. Copyright 2012 from American Chemical Society.

Figure 1-2 (a–c) TEM images of (a) PSPAA-encapsulated CNT bundles, (b) compressed CNT rings with PSPAA shells, (c) circular CNT rings after removal of the PSPAA shell. (d) HRTEM image of CNT bundles in a ring section of (c). Reprinted with permission from ref 30, respectively. Copyright 2011 from American Chemical Society.

Silica has advantages in chemical inertness, optical transparency, porous structure, and size-selective permeability. As a result, it has broad applications in catalysis, separation, sensor technologies, medical materials, bio probes, and optics.^[42-43] A number of reports have been devoted to the preparation of

distinct silica nanostructures, such as spheres,^[44-50] hollow spheres,^[51-54] tubes,^[55-56] complex core-shell colloids,^[57-58] nanowires and nanorods,^[59-65] fibers,^[66-73] mesoporous silica,^[74-87] and helical architectures.^[88-89] The biomimetic strategy is one of the most promising methods in this field. It is achieved by using surfactants or polymers as structure-directing agents. Hence, there are so many complex silica nanostructures can be created, such as plates,^[71, 82] high-aspect-ratio tubules, ribbons with helical architectures,^[89] hybrid mesostructures,^[89-91] doughnuts,^[83] and chiral structures.^[92-94]

1.3 Silica nanoparticle

There are two classes of techniques developed for silica nanoparticle formation: the sol-gel method and the microemulsion method.^[95]

In 1968, Stöber and Fink reported a simple synthesis of monodisperse spherical silica particles by means of hydrolysis of a dilute solution of TEOS in ethanol at high pH as observed earlier by Kolbe.^[50] This Stöber method was later developed by many others and appears to be the simplest and most effective route to synthesize the monodispersed silica spheres.^[96-100]

Microemulsions are macroscopically homogeneous mixtures of water, organic solvent, and surfactant, which on the microscopic level consist of heterogeneous domains of water and organic solvent separated by a surfactant monolayer.^[101] Since microemulsions are thermodynamically stable systems,

both the content of the droplets and the surfactant molecules at the interfaces are constantly and rapidly exchanged between different droplets, thereby facilitating chemical reactions involved in particle synthesis. In 1990, Osseoasare and Arrigada prepared nanosized and monodepersed silica particles by controlled hydrolysis of TEOS in a reverse microemulsion.^[102]

1.4 Silica core-shell structures

Core-shell nanoparticles are gradually attracting more and more attention with modified properties. Silica core-shell structures have advantages as follows: firstly, it reduces the bulk conductivity and increases the suspension stability of the core particles. Secondly, because of the most chemically inertness of silica, it can block the core surface without interfering in the re-dox reaction at the core surface. Thirdly, it can also modulate the position and intensity of the surface Plasmon absorbance band since silica is optically transparent.^[103] Hence, researchers have concentrated more on silica coatings on different inorganic core materials such as metals, binary inorganic composites, metal oxides, and metalsalts.^[104-105] Especially, the metal cores include Au, Ag, Ni, Co, Fe, Fe-Ni and so on.^[103] The silica thickness from 20 to 100 nm can be adjusted by controlling the experimental parameters such as coating time, concentration of reactions, catalyst, and other precursors. Silica-coated magnetite particles are well dispersed and more biocompatible

when used for biological applications.

There are also two methods to synthesize silica core-shell structures: modified Stöber method and microemulsion method.

In 2002, Xia group has coated gold nanoparticles with amorphous silica to form spherical colloids with a core-shell structure (Figure 1-3). By changing the concentration of the TEOS precursor or the coating time, the thickness of silica shells could be adjusted from tens to several hundred nanometers.^[106]

In 2008, Hyeon group synthesized uniformly sized silica-coated magnetic nanoparticles in a simple one-pot process using reverse micelles as nanoreactors (Figure 1-4). By adjusting the ratio of [polar solvent]/[surfactant] in the reverse-micelle solution, the core diameter of the magnetic nanoparticles was easily controlled. And the thickness of the silica shell was easily controlled by varying the amount of TEOS added after the synthesis of the magnetite cores.^[104]

Figure 1-3 (a) Transmission electron microscopy (TEM) image of gold nanoparticles with an average diameter of 50 nm. (b, c) TEM images of such gold nanoparticles after their surfaces had been coated with amorphous silica shells of ~20 and ~80 nm in thickness, respectively. Reprinted with permission from ref 106, respectively. Copyright 2002 from American Chemical Society.

Figure 1-4 Schematic diagram of the one-pot synthesis of uniformly sized silica-coated magnetite nanoparticles. Reprinted with permission from ref 104.

Copyright 2008 from Wiley-VCH Verlag GmbH & Co.

1.5 Hollow silica nanostructure

Owing to the properties of low density, large surface areas, excellent loading capacity, high permeability, and interstitial hollow spaces, hollow silica nanostructures have been widely applied in many important research fields, such as catalysis, controlled release, confined synthesis, optics and electronics, and energy storage. As a special class of hollow silica structure, the interior of hollow silica structures decorated by encapsulating guest species, which are called “yolk-shell” or “rattle” structures, has attracted tremendous interest in recent years. Several synthetic strategies for hollow silica structures have been developed, including well-known hard/soft-templating methods,^[107-118]

self-templating methods,^[119] ship-in-bottle techniques,^[120] and selective etching.^[121-124]

In 2008, Yin group reported that amorphous silica colloids underwent a spontaneous morphology change from solid to hollow spheres by dispersing in an aqueous solution of NaBH_4 (Figure 1-5). The formation of the hollow structures was supposed to come from concurrent but separate core-dissolution and shell-growth processes.^[119]

Zheng group reported that hollow/yolk-shell structures could be prepared by using silica spheres as the silica precursors. By treating with a hot alkaline solution in the presence of sodium aluminate and CTAB, solid silica spheres converted into hollow mesoporous aluminosilica spheres with perpendicular pore channels under the mechanism of etching followed by co-assembly.^[125]

Shi group reported a “structural difference-based selective etching” strategy to fabricate hollow/rattle-type silica nanostructures. It was achieved by using the structural differences between the core and the shell of a silica core/mesoporous silica shell structure to create hollow interiors.^[126]

Figure 1-5 (a) Schematic illustration of the spontaneous formation of hollow SiO_2 spheres. (b) TEM images of as-prepared SiO_2 spheres. (c, d) Samples after reacting with 0.06 g/mL NaBH_4 for 6 h at 51°C (c), and 5 h at 56°C (d). Scale bars are 200 nm. Reprinted with permission from ref 119. Copyright 2008 from Wiley-VCH Verlag GmbH & Co.

Figure 1-6 (a-d) TEM images of the morphological evolution in the time-dependent experiments: (a) 0.5h, (b) 1h, (c) 2h, (d) 3h. (e, f) TEM images of the products obtained by the addition of Fe_2O_3 particles. (g) Schematic illustration for the formation of the hollow mesoporous aluminosilica spheres: (I) alkaline etching of silica template, (II) co-assembly of cationic surfactant, aluminous species, and silica species. Reprinted with permission from ref 125, respectively. Copyright 2012 from American Chemical Society.

Figure 1-7 Formation schematics of hollow/rattle-type mesoporous silica spheres (left) and the microscopic structure schematics (right). Route A represents the selective-etching procedure in Na_2CO_3 solution and route B for that in ammonia solution under hydrothermal treatment. The local microscopic structure of the right part shows that there exist hydrophobic cores formed by the long carbon chains of C_{18}TMS , which is the pore-making area after burning out the organic carbon chains. The more open structure of the shell facilitates the penetration of the OH^- ions to selectively etch the core part. Reprinted with permission from ref 126, respectively. Copyright 2010 from American Chemical Society.

Figure 1-8 Strategy to modulate the void space in yolk-shell NPs. TEM images of (a) AuNP@silica with one hardened silica shell and yolk-shell NPs with small void space (b) before and (c) after coating of an additional shell. (d–f) TEM images of similar nanostructures derived from Au NP @ silica with three soft spacer shells. (g, h) Schematics and TEM images of nano-matryoshkas. Scale bars = 50 nm. Reprinted with permission from ref 121, respectively. Copyright 2011 from American Chemical Society.

Our group demonstrated that the silica shell on nanoparticles formed by stöber method is inhomogeneous in nature. The outer layer of the shell is chemically more robust than the inner layer, which can be selectively etched by hot water to fabricate sophisticated yolk-shell nanostructures (Figure 1-8).^[121]

1.6 Mesoporous silica nanoparticle

MCM-41 and SBA-15 are the most common types of mesoporous silica nanoparticles. They have applications in catalysis, drug delivery, imaging and biomedicine because of uniform mesopores, easy functionalization and significant biocompatibility.^[127-129] The silica framework, the nanochannels/pores, and the nanoparticle outermost surface can be independently functionalized. Many possible modalities on mesoporous silica nanoparticles are available for high loading of fluorescent or MRI contrast agents, giving site-specific targeting ability for intracellular delivery,^[130] and containers for drugs, DNA or RNA delivery.^[131-132]

The novel family of molecular sieves called M41S was the pioneer of mesoporous silica. It was reported by the researchers at Mobil Research and Development Corporation in 1992.^[133] The M41S materials have uniform pore sizes greater than 20 Å, surface areas in excess of 1000 m²g⁻¹, and long-range ordering of the packing of pores. The synthesis of those mesoporous silica relies upon surfactant micelles as templates for the assembly and subsequent

condensation of silica precursors. The mesostructure depended on the hydrocarbon chain length of the surfactant tail group, the effect of variation of the surfactant concentrations, and the influence of organic swelling agents.^[134] All the three classes of surfactants (cationic, anionic, and nonionic) have been used in the synthesis the mesoporous silica.^[135] Based on the electrostatic interactions between cationic quaternary ammonium surfactants and silica precursors, the well-ordered hexagonal, cubic, and lamellar mesoporous silica (M41S family and SBA-1, -2, -3, -7, etc.) have been prepared under both basic and acidic conditions.^[133, 136-137] Due to hydrogen bonding or electrostatic interactions, neutral nonionic surfactants (block copolymers) were used as templates to prepare mesoporous materials with large pores (HMS, SBA-11, -12, -15, -16 and FDU-1, -2, -5 etc.).^[138-139] Che group has reported the new anionic surfactant templating route to mesoporous silica by introducing an additional structure-directing effect by inclusion of aminopropylsiloxane or quaternized aminopropylsiloxane in the silica precursors.^[135]

Based on the similarity between liquid crystalline surfactant assemblies and M41S, a “liquid crystal templating” (LCT) mechanism was proposed by the Mobil researchers. The two main pathways of cooperative self-assembly and “true” liquid-crystal templating processes seem to be effective in the synthesis of ordered mesostructures.^[140]

Figure 1-9 Two synthetic strategies of mesoporous materials: (a) cooperative self-assembly; (b) “true” liquid-crystal templating process. Reprinted with permission from ref 140, respectively. Copyright 2007 from American Chemical Society.

1.7 Helical mesoporous silica nanostructure

In 2004, Che reported the chiral surfactant-templated synthesis of ordered chiral mesoporous silica with a twisted hexagonal rod-like morphology. Transmission electron microscopy combined with computer simulations confirm the presence of hexagonally ordered chiral channels of 2.2 nm diameter winding around the central axis of the rods. In the product, there were more left-handed helices than right-handed ones (about 30% ee).^[141] Following this paper, a number of papers reported the synthesis of similar chiral rods of mesoporous silica, but the starting surfactants and silica precursors were all achiral (Figure. 1-10).^[142-146]

The product was racemic containing both left- and right-handed twisted rods. The central channels of such rods were straight, but the surrounding channels have helical configurations; their curvature increased with increasing distance from the central channel (Figure. 1-11a).^[147] The overall pitch length and the degree of twisting were found to correlate with the size of the rods.^[142, 144] When chiral surfactants were used, the ee of the resulting rods increased, but it never reached 100%.^[148]

Three mechanisms have been put forward: Che and Qiu proposed that the progressively staggered stacking of the surfactant molecules forced the resulting cylindrical micelles to twist into helices.^[149] The twisting of such individual cylinders was in turn the cause for the overall twisting of the mesoporous rods. Thus, when chiral surfactants were used, the twisting of the cylinders was biased towards a particular direction, leading to a non-zero ee. Zhao and co-workers proposed that the main driving force was the minimization of the silica/solvent interfacial energy. When a hexagonal bundle of straight cylindrical micelles was twisted into a helical bundle, the reduction of the surface to volume ratio (S/V) was estimated to be 5.2–6% (Figure. 1-11c and d). Han and co-workers proposed that the twisting of the cylinder bundles was driven by entropy: the depleting interaction of external species (ammonia, etc.) forced the bundles into a more compact helical configuration.^[144, 150]

Figure 1-10 SEM and TEM images of the chiral mesoporous silica formed by the co-assembly of chiral surfactants and silica; (c) SEM images of the typical helices formed by the co-assembly of achiral CTAB and silica; and (d) TEM images of two intertwined strands of mesoporous silica, which was formed by the co-assembly of achiral surfactant SDS, positively charged N-tri-methoxysilylpropyl-N,N,N,-trimethylammonium ions, and TEOS. Reprinted with permission from ref. 141–143, respectively. Copyright 2004 from Nature Publishing group; 2007 from Wiley-VCH Verlag GmbH & Co.; and 2006 from American Chemical Society.

Figure 1-11 Schematics illustrating (a) the configuration of the chiral channels in a mesoporous silica rod; (b) the helical stacking of amphiphiles with chiral heads; and (c) the twisting of hexagonally arrayed rod-like micelles to form a helical rod, driven by the reduction in overall S/V. (d) TEM image of a chiral mesoporous silica rod, highlighting its rounded ends. Reprinted with permission from ref. 143, 148 and 149, respectively. Copyright 2005 from Wiley-VCH Verlag GmbH & Co., as well as copyright 2006 and 2008 from American Chemical Society.

1.8 Silica vesicle

Usually, silica vesicle comes from the interaction between pre-existing vesicle template of surfactant and silica precursor.

Hubert first reported the synthesis of unilamellar silica vesicles from vesicle templating of cationic surfactants by directly coating the pre-existing unilamellar vesicles with silica.^[151]

In 1998, ultrastable mesostructured silica vesicle was prepared through a supermolecular assembly pathway that relies on hydrogen bonding between electrically neutral Gemini surfactant of the type $C_nH_{2n+1}NH(CH_2)_2NH_2$ and silica precursors derived from TEOS.^[152]

1.9 Bibliography

- [1] C. Buzea, I. Pacheco, K. Robbie, *Biointerphases* **2007**, 2, MR17-MR71.
- [2] C. G. Levins, C. E. Schafmeister, *ChemInform* **2006**, 37,(5).
10.1002/chin.200605222
- [3] S. Das, A. J. Gates, H. A. Abdu, G. S. Rose, C. A. Picconatto, J. C. Ellenbogen, *Circuits and Systems I: Regular Papers, IEEE Transactions on* **2007**, 54, 2528-2540.
- [4] S. Mashaghi, T. Jadidi, G. Koenderink, A. Mashaghi, *International Journal of Molecular Sciences* **2013**, 14, 4242-4282.

- [5] Z. Ghalanbor, S.-A. Marashi, B. Ranjbar, *Medical hypotheses* **2005**, *65*, 198-199.
- [6] R. C. Shetty, *Medical hypotheses* **2005**, *65*, 998-999.
- [7] J. Chen, J. M. McLellan, A. Siekkinen, Y. Xiong, Z.-Y. Li, Y. Xia, *J. Am. Chem. Soc.* **2006**, *128*, 14776-14777.
- [8] S. E. Skrabalak, J. Chen, Y. Sun, X. Lu, L. Au, C. M. Cobley, Y. Xia, *Acc. Chem. Res* **2008**, *41*, 1587-1595.
- [9] J. Chen, F. Saeki, B. J. Wiley, H. Cang, M. J. Cobb, Z.-Y. Li, L. Au, H. Zhang, M. B. Kimmey, Li, Y. Xia, *Nano Lett.* **2005**, *5*, 473-477.
- [10] D. Li, Y. Xia, *Adv. Mater.* **2004**, *16*, 1151-1170.
- [11] Z.-M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, *Composites Science and Technology* **2003**, *63*, 2223-2253.
- [12] A. Narayanaswamy, H. Xu, N. Pradhan, M. Kim, X. Peng, *J. Am. Chem. Soc.* **2006**, *128*, 10310-10319.
- [13] K. E. Martin, Z. Wang, T. Busani, R. M. Garcia, Z. Chen, Y. Jiang, Y. Song, J. L. Jacobsen, T. T. Vu, N. E. Schore, B. S. Swartzentruber, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2010**, *132*, 8194-8201.
- [14] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, J. Osterwalder, *Science* **2004**, *303*, 217-220.
- [15] S. Berner, M. Corso, R. Widmer, O. Groening, R. Laskowski, P. Blaha, K. Schwarz, A. Goriachko, H. Over, S. Gsell, M. Schreck, H. Sachdev, T.

- Greber, J. Osterwalder, *Angew. Chem. Int. Ed.* **2007**, *46*, 5115-5119.
- [16] R. Laskowski, P. Blaha, T. Gallauner, K. Schwarz, *Phys. Rev. Lett.* **2007**, *98*, 106802, 1-4.
- [17] C. G. Granqvist, R. A. Buhrman, J. Wyns, A. J. Sievers, *Phys. Rev. Lett.* **1976**, *37*, 625-629.
- [18] C. J. Murphy, *Science* **2002**, *298*, 2139-2141.
- [19] G. Whitesides, J. Mathias, C. Seto, *Science* **1991**, *254*, 1312-1319.
- [20] J. Belloni, M. Mostafavi, H. Remita, J.-L. Marignier, a. Marie-Odile Delcourt, *New J. Chem.* **1998**, *22*, 1239-1255.
- [21] L. L. Hench, J. K. West, *Chem. Rev.* **1990**, *90*, 33-72.
- [22] Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176-2179.
- [23] K.-M. Sung, D. W. Mosley, B. R. Peelle, S. Zhang, J. M. Jacobson, *J. Am. Chem. Soc.* **2004**, *126*, 5064-5065.
- [24] F. J. Duarte, R. O. James, *Opt. Lett.* **2003**, *28*, 2088-2090.
- [25] H. Sun, X. Shen, L. Yao, S. Xing, H. Wang, Y. Feng, H. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 11243-11250.
- [26] H. Sun, J. He, J. Wang, S.-Y. Zhang, C. Liu, T. Sritharan, S. Mhaisalkar, M.-Y. Han, D. Wang, H. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 9099-9110.
- [27] Y. Feng, Y. Wang, H. Wang, T. Chen, Y. Y. Tay, L. Yao, Q. Yan, S. Li, H. Chen, *Small* **2012**, *8*, 246-251.

- [28] X. Y. Kong, Y. Ding, R. Yang, Z. L. Wang, *Science* **2004**, *303*, 1348-1351.
- [29] J. Xu, H. Wang, C. Liu, Y. Yang, T. Chen, Y. Wang, F. Wang, X. Liu, B. Xing, H. Chen, *J. Am. Chem. Soc.* **2010**, *132*, 11920-11922.
- [30] L. Chen, H. Wang, J. Xu, X. Shen, L. Yao, L. Zhu, Z. Zeng, H. Zhang, H. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 9654-9657.
- [31] L. Chen, S. Yu, H. Wang, J. Xu, C. Liu, W. H. Chong, H. Chen, *J. Am. Chem. Soc.* **2012**, *135*, 835-843.
- [32] D. V. Talapin, E. V. Shevchenko, C. B. Murray, A. Kornowski, S. Förster, H. Weller, *J. Am. Chem. Soc.* **2004**, *126*, 12984-12988.
- [33] X. Huang, S. Neretina, M. A. El-Sayed, *Adv. Mater.* **2009**, *21*, 4880-4910.
- [34] J. B. Rivest, P. K. Jain, *Chem. Soc. Rev* **2013**, *42*, 89-96.
- [35] D. Seo, H. Song, *J. Am. Chem. Soc.* **2009**, *131*, 18210-18211.
- [36] B. E. Brinson, J. B. Lassiter, C. S. Levin, R. Bardhan, N. Mirin, N. J. Halas, *Langmuir* **2008**, *24*, 14166-14171.
- [37] S. Duraiswamy, S. A. Khan, *Nano Lett.* **2010**, *10*, 3757-3763.
- [38] R. Hushka, J. Zuloaga, M. W. Knight, L. V. Brown, P. Nordlander, N. J. Halas, *J. Am. Chem. Soc.* **2011**, *133*, 12247-12255.
- [39] M. José-Yacamán, L. Rendón, J. Arenas, M. C. S. Puche, *Science* **1996**, *273*, 223-225.

- [40] E. Manias, *Nat Mater* **2007**, 6, 9-11.
- [41] G. A. Sotiriou, C. O. Blattmann, S. E. Pratsinis, *Adv. Funct. Mater.* **2013**, 23, 34-41.
- [42] N. K. Raman, M. T. Anderson, C. J. Brinker, *Chem. Mater.* **1996**, 8, 1682-1701.
- [43] X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu, K. M. Kemner, *Science* **1997**, 276, 923-926.
- [44] J. H. Zhang, P. Zhan, Z. L. Wang, W. Y. Zhang, N. B. Ming, *J. Mater. Res* **2003**, 18, 649-653.
- [45] T. Yanagishita, Y. Tomabechi, K. Nishio, H. Masuda, *Langmuir* **2004**, 20, 554-555.
- [46] M. Sumper, S. Lorenz, E. Brunner, *Angew. Chem. Int. Ed.* **2003**, 42, 5192-5195.
- [47] J. J. Yuan, R. H. Jin, *Adv. Mater.* **2005**, 17, 885-888.
- [48] M. M. Tomczak, D. D. Glawe, L. F. Drummy, C. G. Lawrence, M. O. Stone, C. C. Perry, D. J. Pochan, T. J. Deming, R. R. Naik, *J. Am. Chem. Soc.* **2005**, 127, 12577-12582.
- [49] D. D. Glawe, F. Rodríguez, M. O. Stone, R. R. Naik, *Langmuir* **2004**, 21, 717-720.
- [50] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, 26, 62-69.
- [51] F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, 282, 1111-1114.

- [52] A. Khanal, Y. Inoue, M. Yada, K. Nakashima, *J. Am. Chem. Soc.* **2007**, *129*, 1534-1535.
- [53] M. Fujiwara, K. Shiokawa, I. Sakakura, Y. Nakahara, *Nano Lett.* **2006**, *6*, 2925-2928.
- [54] C. A. Bauer, D. B. Robinson, B. A. Simmons, *Small* **2007**, *3*, 58-62.
- [55] B. Yao, D. Fleming, M. A. Morris, S. E. Lawrence, *Chem. Mater.* **2004**, *16*, 4851-4855.
- [56] K. J. C. v. Bommel, J. H. Jung, S. Shinkai, *Adv. Mater.* **2001**, *13*, 1472-1476.
- [57] S. H. Liu, M. Y. Han, *Adv. Funct. Mater.* **2005**, *15*, 961-967.
- [58] J. Zhang, J. Liu, S. Wang, P. Zhan, Z. Wang, N. Ming, *Adv. Funct. Mater.* **2004**, *14*, 1089-1096.
- [59] C. Yu, J. Fan, B. Tian, D. Zhao, G. D. Stucky, *Adv. Mater.* **2002**, *14*, 1742-1745.
- [60] Z. Yang, Z. Niu, X. Cao, Z. Yang, Y. Lu, Z. Hu, C. C. Han, *Angew. Chem. Int. Ed.* **2003**, *42*, 4201-4203.
- [61] S. Giri, B. G. Trewyn, M. P. Stellmaker, V. S. Y. Lin, *Angew. Chem. Int. Ed.* **2005**, *44*, 5038-5044.
- [62] S. J. Limmer, G. Cao, *Adv. Mater.* **2003**, *15*, 427-431.
- [63] D. P. Yu, Q. L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, S. Q. Feng, *Appl. Phys. Lett.* **1998**, *73*,

3076-3078.

- [64] A. Sayari, B.-H. Han, Y. Yang, *J. Am. Chem. Soc.* **2004**, *126*, 14348-14349.
- [65] Z. Zhang, J. Buitenhuis, *Small* **2007**, *3*, 424-428.
- [66] S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky, F. Schüth, *Science* **1996**, *273*, 768-771.
- [67] P. J. Bruinsma, A. Y. Kim, J. Liu, S. Baskaran, *Chem. Mater.* **1997**, *9*, 2507-2512.
- [68] F. Kleitz, F. Marlow, G. D. Stucky, F. Schüth, *Chem. Mater.* **2001**, *13*, 3587-3595.
- [69] F. Marlow, M. D. McGehee, D. Zhao, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1999**, *11*, 632-636.
- [70] J. Wang, J. Zhang, B. Y. Asoo, G. D. Stucky, *J. Am. Chem. Soc.* **2003**, *125*, 13966-13967.
- [71] P.-X. Zhu, N. Fukazawa, R.-H. Jin, *Small* **2007**, *3*, 394-398.
- [72] J. J. Yuan, P. X. Zhu, N. Fukazawa, R. H. Jin, *Adv. Funct. Mater.* **2006**, *16*, 2205-2212.
- [73] R.-H. Jin, J.-J. Yuan, *Chem. Mater.* **2006**, *18*, 3390-3396.
- [74] H. Yang, N. Coombs, G. A. Ozin, *Nature* **1997**, *386*, 692-695.
- [75] H. Song, R. M. Rioux, J. D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P. Yang, G. A. Somorjai, *J. Am. Chem. Soc.* **2006**, *128*,

3027-3037.

- [76] K. Flodström, V. Alfredsson, N. Källrot, *J. Am. Chem. Soc.* **2003**, *125*, 4402-4403.
- [77] K. Suzuki, K. Ikari, H. Imai, *J. Am. Chem. Soc.* **2003**, *126*, 462-463.
- [78] T.-W. Kim, F. Kleitz, B. Paul, R. Ryoo, *J. Am. Chem. Soc.* **2005**, *127*, 7601-7610.
- [79] Y. Li, W. T. Yip, *J. Am. Chem. Soc.* **2005**, *127*, 12756-12757.
- [80] A. P. Z. Clark, K.-F. Shen, Y. F. Rubin, S. H. Tolbert, *Nano Lett.* **2005**, *5*, 1647-1652.
- [81] J. Lee, J. Kim, J. Kim, H. Jia, M. I. Kim, J. H. Kwak, S. Jin, A. Dohnalkova, H. G. Park, H. N. Chang, P. Wang, J. W. Grate, T. Hyeon, *Small* **2005**, *1*, 744-753.
- [82] P. Feng, X. Bu, G. D. Stucky, D. J. Pine, *J. Am. Chem. Soc.* **1999**, *122*, 994-995.
- [83] D. Zhao, J. Sun, Q. Li, G. D. Stucky, *Chem. Mater.* **2000**, *12*, 275-279.
- [84] P. Yang, D. Zhao, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* **1998**, *10*, 2033-2036.
- [85] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024-6036.
- [86] D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1998**, *10*, 1380-1385.

- [87] J. Wang, C.-K. Tsung, W. Hong, Y. Wu, J. Tang, G. D. Stucky, *Chem. Mater.* **2004**, *16*, 5169-5181.
- [88] S. M. Yang, I. Sokolov, N. Coombs, C. T. Kresge, G. A. Ozin, *Adv. Mater.* **1999**, *11*, 1427-1431.
- [89] A. M. Seddon, H. M. Patel, S. L. Burkett, S. Mann, *Angew. Chem. Int. Ed.* **2002**, *41*, 2988-2991.
- [90] C. G. Göltner, S. Henke, M. C. Weissenberger, M. Antonietti, *Angew. Chem. Int. Ed.* **1998**, *37*, 613-616.
- [91] J. Fan, C. Yu, F. Gao, J. Lei, B. Tian, L. Wang, Q. Luo, B. Tu, W. Zhou, D. Zhao, *Angew. Chem. Int. Ed.* **2003**, *42*, 3146-3150.
- [92] B. Wang, C. Chi, W. Shan, Y. Zhang, N. Ren, W. Yang, Y. Tang, *Angew. Chem. Int. Ed.* **2006**, *45*, 2088-2090.
- [93] H. Jin, Z. Liu, T. Ohsuna, O. Terasaki, Y. Inoue, K. Sakamoto, T. Nakanishi, K. Ariga, S. Che, *Adv. Mater.* **2006**, *18*, 593-596.
- [94] J. Zhang, H. Liu, Z. Wang, N. Ming, *Chem. Eur. J.* **2008**, *14*, 4374-4380.
- [95] M. Darbandi, R. Thomann, T. Nann, *Chem. Mater.* **2007**, *19*, 1700-1703.
- [96] A. K. Van Helden, J. W. Jansen, A. Vrij, *J. Colloid Interface Sci.* **1981**, *81*, 354-368.
- [97] A. P. Philipse, *Colloid & Polymer Sci* **1988**, *266*, 1174-1180.
- [98] A. P. Philipse, A. Vrij, *J. Colloid Interface Sci.* **1989**, *128*, 121-136.
- [99] G. H. Bogush, M. A. Tracy, C. F. Zukoski Iv, *J. Noncryst. Sol.* **1988**, *104*,

95-106.

- [100] A. van Blaaderen, A. Vrij, *J. Colloid Interface Sci.* **1993**, *156*, 1-18.
- [101] A. Guerrero-Martínez, J. Pérez-Juste, L. M. Liz-Marzán, *Adv. Mater.* **2010**, *22*, 1182-1195.
- [102] K. Osseo-Asare, F. J. Arriagada, *Colloids and Surfaces* **1990**, *50*, 321-339.
- [103] R. Ghosh Chaudhuri, S. Paria, *Chem. Rev.* **2011**, *112*, 2373-2433.
- [104] J. Lee, Y. Lee, J. K. Youn, H. B. Na, T. Yu, H. Kim, S.-M. Lee, Y.-M. Koo, J. H. Kwak, H. G. Park, H. N. Chang, M. Hwang, J.-G. Park, J. Kim, T. Hyeon, *Small* **2008**, *4*, 143-152.
- [105] F. G. Aliev, M. A. Correa-Duarte, A. Mamedov, J. W. Ostrander, M. Giersig, L. M. Liz-Marzán, N. A. Kotov, *Adv. Mater.* **1999**, *11*, 1006-1010.
- [106] Y. Lu, Y. Yin, Z.-Y. Li, Y. Xia, *Nano Lett.* **2002**, *2*, 785-788.
- [107] K. Kamata, Y. Lu, Y. Xia, *J. Am. Chem. Soc.* **2003**, *125*, 2384-2385.
- [108] P. M. Arnal, M. Comotti, F. Schüth, *Angew. Chem. Int. Ed.* **2006**, *45*, 8224-8227.
- [109] J. Lee, J. C. Park, H. Song, *Adv. Mater.* **2008**, *20*, 1523-1528.
- [110] X. Huang, C. Guo, J. Zuo, N. Zheng, G. D. Stucky, *Small* **2009**, *5*, 361-365.
- [111] J. Park, H. Song, *Nano Res.* **2011**, *4*, 33-49.

- [112] S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, *Angew. Chem. Int. Ed.* **2006**, *45*, 7063-7066.
- [113] K. M. Yeo, S. Choi, R. M. Anisur, J. Kim, I. S. Lee, *Angew. Chem. Int. Ed.* **2011**, *50*, 745-748.
- [114] X. W. Lou, C. Yuan, L. A. Archer, *Adv. Mater.* **2007**, *19*, 3328-3332.
- [115] J. Liu, S. Z. Qiao, S. Budi Hartono, G. Q. Lu, *Angew. Chem. Int. Ed.* **2010**, *49*, 4981-4985.
- [116] W. Li, Y. Deng, Z. Wu, X. Qian, J. Yang, Y. Wang, D. Gu, F. Zhang, B. Tu, D. Zhao, *J. Am. Chem. Soc.* **2011**, *133*, 15830-15833.
- [117] W.-M. Zhang, J.-S. Hu, Y.-G. Guo, S.-F. Zheng, L.-S. Zhong, W.-G. Song, L.-J. Wan, *Adv. Mater.* **2008**, *20*, 1160-1165.
- [118] X.-J. Wu, D. Xu, *Adv. Mater.* **2010**, *22*, 1516-1520.
- [119] T. Zhang, J. Ge, Y. Hu, Q. Zhang, S. Aloni, Y. Yin, *Angew. Chem. Int. Ed.* **2008**, *47*, 5806-5811.
- [120] S. Ding, J. S. Chen, G. Qi, X. Duan, Z. Wang, E. P. Giannelis, L. A. Archer, X. W. Lou, *J. Am. Chem. Soc.* **2010**, *133*, 21-23.
- [121] Y. J. Wong, L. Zhu, W. S. Teo, Y. W. Tan, Y. Yang, C. Wang, H. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 11422-11425.
- [122] Q. Zhang, I. Lee, J. Ge, F. Zaera, Y. Yin, *Adv. Funct. Mater.* **2010**, *20*, 2201-2214.

- [123] Y. Chen, H. Chen, L. Guo, Q. He, F. Chen, J. Zhou, J. Feng, J. Shi, *ACS Nano* **2009**, *4*, 529-539.
- [124] X. Fang, C. Chen, Z. Liu, P. Liu, N. Zheng, *Nanoscale* **2011**, *3*, 1632-1639.
- [125] X. Fang, Z. Liu, M.-F. Hsieh, M. Chen, P. Liu, C. Chen, N. Zheng, *ACS Nano* **2012**, *6*, 4434-4444.
- [126] Y. Chen, H. Chen, L. Guo, Q. He, F. Chen, J. Zhou, J. Feng, J. Shi, *ACS Nano* **2009**, *4*, 529-539.
- [127] S.-H. Wu, Y. Hung, C.-Y. Mou, *Chem. Commun.* **2011**, *47*, 9972-9985.
- [128] B. G. Trewyn, S. Giri, I. I. Slowing, V. S. Y. Lin, *Chem. Commun.* **2007**, 3236-3245.
- [129] Q. He, J. Shi, *J. Mater. Chem.* **2011**, *21*, 5845-5855.
- [130] L. Y. T. Chou, K. Ming, W. C. W. Chan, *Chem. Soc. Rev* **2011**, *40*, 233-245.
- [131] M. Manzano, M. Vallet-Regi, *J. Mater. Chem.* **2010**, *20*, 5593-5604.
- [132] M.-H. Kim, H.-K. Na, Y.-K. Kim, S.-R. Ryoo, H. S. Cho, K. E. Lee, H. Jeon, R. Ryoo, D.-H. Min, *ACS Nano* **2011**, *5*, 3568-3576.
- [133] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.
- [134] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem. Int. Ed.* **1999**, *38*,

56-77.

- [135] C. Gao, H. Qiu, W. Zeng, Y. Sakamoto, O. Terasaki, K. Sakamoto, Q. Chen, S. Che, *Chem. Mater.* **2006**, *18*, 3904-3914.
- [136] Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 1147-1160.
- [137] C. C. Pantazis, P. J. Pomonis, *Chem. Mater.* **2003**, *15*, 2299-2300.
- [138] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024-6036.
- [139] C. Yu, B. Tian, J. Fan, G. D. Stucky, D. Zhao, *J. Am. Chem. Soc.* **2002**, *124*, 4556-4557.
- [140] Y. Wan, Zhao, *Chem. Rev.* **2007**, *107*, 2821-2860.
- [141] S. Che, Z. Liu, T. Ohsuna, K. Sakamoto, O. Terasaki, T. Tatsumi, *Nature* **2004**, *429*, 281-284.
- [142] S. Yang, L. Zhao, C. Yu, X. Zhou, J. Tang, P. Yuan, D. Chen, D. Zhao, *J. Am. Chem. Soc.* **2006**, *128*, 10460-10466.
- [143] B. Wang, C. Chi, W. Shan, Y. Zhang, N. Ren, W. Yang, Y. Tang, *Angew. Chem. Int. Ed.* **2006**, *45*, 2088-2090.
- [144] Y. Han, L. Zhao, J. Y. Ying, *Adv. Mater.* **2007**, *19*, 2454-2459.
- [145] X. Wu, H. Jin, Z. Liu, T. Ohsuna, O. Terasaki, K. Sakamoto, S. Che, *Chem. Mater.* **2005**, *18*, 241-243.
- [146] B. G. Trewyn, C. M. Whitman, V. S. Y. Lin, *Nano Lett.* **2004**, *4*,

2139-2143.

- [147] T. Ohsuna, Z. Liu, S. Che, O. Terasaki, *Small* **2005**, *1*, 233-237.
- [148] H. Qiu, S. Wang, W. Zhang, K. Sakamoto, O. Terasaki, Y. Inoue, S. Che, *J. Phys. Chem. C* **2008**, *112*, 1871-1877.
- [149] H. Qiu, S. Che, *J. Phys. Chem, B* **2008**, *112*, 10466-10474.
- [150] Y. Snir, R. D. Kamien, *Science* **2005**, *307*, 1067.
- [151] D. H. W. Hubert, M. Jung, P. M. Frederik, P. H. H. Bomans, J. Meuldijk, A. L. German, *Adv. Mater.* **2000**, *12*, 1286-1290.
- [152] S. S. Kim, W. Zhang, T. J. Pinnavaia, *Science* **1998**, *282*, 1302-1305.

Chapter 2 Bilayer Silica Vesicles: Understanding the Cylinder-to-Vesicle Phase Transition of Mesoporous Silica

2.1 Introduction

Vesicles are synthetic nano-compartments that have a great promise in catalysis and drug delivery.^[1-2] However, they are typically assembled from organic surfactants and thus, often too soft and unstable for application in harsh environments. On the other hand, mesoporous silica is a hard material derived from the co-assembly of silica with surfactants,^[3-8] thus providing an inorganic alternative of nano-compartments.^[9-11] But it cannot be readily tuned, unlike the soft surfactant micelles that are known for the easy transition from spheres to cylinders and to vesicles.^[12-14]

Mesoporous silica has been extensively explored for industrial applications such as separation and catalysis.^[15-16] A famous type is the Mobil Composition of Matter No. 41 (MCM-41), which is derived from the hexagonally packed cylindrical phase of hexadecyltrimethylammonium bromide (CTAB).^[15] Despite intensive research, how the cylindrical MCM-41 phase arises from the complex interactions among the ingredients is still not well understood.

MCM-41 can be converted to MCM-48 and lamellar phases at high temperature ($> 100\text{ }^{\circ}\text{C}$).^[17] Vesicular phase of mesoporous silica has also been synthesized,^[18-21] but the transition between the cylindrical and vesicular phases has been much less studied. Exploring such a transition would provide a window for understanding the complex interactions during the phase selection, and thus, the differences and similarities between the assembly of pure surfactants and the co-assembly of silica with surfactants.^[22-23]

Without silica involvement, the assembly of CTAB is well-behaved in terms of micellar morphology and phase outcome. As characterized by cryogenic transmission electron microscopy (cryo-TEM), the phase transition from spheres to cylinders and then to vesicles has been demonstrated by doping the micelles with amphiphilic phenolic compounds, which were proposed to reduce the repulsion among the headgroups of CTAB.^[15-16, 22-23] However, the formation of hard silica during surfactant-silica co-assembly would reduce molecular diffusion and micellar mobility, causing a major disturbance that cannot be overlooked. Among the many problems of this complex co-assembly process, the time sequence of micelle assembly and silica formation during the synthesis of MCM-41 has being hotly debated in the literature.

Hence, an ideal system for studying the complex interactions of the ingredients is to generate different phases of mesoporous silica in the same system,^[21, 24] so that one can compare their controlling factors to reveal the

underlying interactions. Such studies are rare and challenging: Yu group found an important factor, namely the ratio of surfactant (CTAB or amphiphilic polymer) to fluorocarbon co-surfactant.^[21] Its effects have been studied in detail; the fluorocarbon increased the packing parameter^[25] of the surfactant, transforming the resulting mesoporous silica from cylindrical to vesicular phase. To expand the study, we seek multiple controlling factors to study their inter-dependence, which is a key indication for the holistic phase behavior. In the assembly of pure surfactant, the controlling factors are not isolated, but interact strongly with each other in determining the outcome of phases. This has not been demonstrated in the phase control of mesoporous silica. Thus, whether the governing principles of soft micelles are modified in hard mesoporous silica remains an open question.

Previously, our group studied the cylinder-to-vesicle transition of polymer micelles.^[13-14] To apply the knowledge to mesoporous silica, we adapted the facile synthesis of MCM-41 from the Qiao group to trap intermediates.^[26] In this report, we explore the inter-dependence of three controlling factors of CTAB-silica micelles to probe the complex interactions among the ingredients: (a) degree of swelling; (b) amount of co-surfactant; and (c) control of composition by diffusion. In this system, cylindrical or vesicular phase directly emerges from the “clumps” of randomly mixed surfactant, co-surfactant, and silica precursor. The phase outcome depends on the exact ratio of these

ingredients and is sensitive to even slight differences. We show that the phase outcome of the clumps can be altered after their formation, provided that enough amount of co-surfactant can reach a particular location before the hardening silica prevents its diffusion.

2.2 Materials and Methods

2.2.1 Materials

All materials were used without further purification. Tetraethoxysilane (TEOS, 99.9%) and (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%) were purchased from Alfa Aesar; Sodium hydroxide (NaOH) was purchased from Sinopharm; 1,3,5-trimethylbenzene (TMB, 98%) and hexadecyltrimethylammonium bromide (CTAB, 99%) were purchased from Sigma Aldrich. Copper specimen grids (300 meshes) with formvar/carbon purchased from Beijing XXBR Technology Co.. Deionized (DI) water (resistance > 18.2 MΩ.cm-1) was used in all of our experiments. Transmission electron microscopy (TEM) images were taken from a JEM-1400 transmission electron microscopy (JEOL) operated at 100 kV. Ultrasonic system was SONOSWISS SW3H from Biofrontier Technology.

2.2.2 Methods

Synthesis of mesoporous silica nanoparticles (use coordinate (0.86, 0.016) as an example). 14 µl of 2 M aqueous NaOH solution was added to a vial

containing 4 mg of CTAB (0.011 mmol) in 2 mL water. The solution was maintained at 80 °C with stirring (750 rpm) until CTAB is completely dissolved. 120 µl of neat TMB (0.86 mmol) was dispersed in this solution, forming a milky white emulsion. After being stirred for 1 min, 45 µl of neat TEOS (0.20 mmol) and 3 µl of neat MPTMS (0.016 mmol) were mixed and added to the above solution. The mixture was stirred at 80 °C for 1h, and the product was isolated by centrifugation and characterized.

Synthesis of mesoporous silica nanoparticles (at other coordinates): the procedures were the same as above, except that different amounts of TMB and MPTMS were used.

Synthesis of mesoporous silica nanoparticles with delayed MPTMS addition: the same procedures were used, except that MPTMS addition was delayed for a certain period ($t = 30$ or 60 s) after the addition of TEOS.

Synthesis of monolayer silica nanoparticles by using sonication: After mixing the ingredients using the above method, the mixture was sonicated at room temperature for 1 h, and the product was isolated by centrifugation and characterized.

2.3 Results and Discussions

2.3.1 Phase diagram summarizing the cylinder-to-vesicle transition of mesoporous silica.

The method developed by the Qiao group was originally used for the synthesis of helical mesoporous silica.^[26] Because it requires neither high temperature nor autoclave, it is ideal for our mechanistic study. We introduced 1, 3, 5-trimethylbenzene (TMB) as an additional controlling factor: CTAB (0.011 mmol) was dissolved in aqueous NaOH solution (0.028 mmol, 2 mL), which was maintained at 80 °C with stirring. TMB (1.44 mmol) was dispersed in this solution, forming a milky-white emulsion in the presence of the surfactant CTAB. After being stirred for 1 min, tetraethoxysilane (TEOS, 0.20 mmol neat) was added to initiate silica formation ($t = 0$). After a given period of time ($t = 0 - 60$ s), the co-surfactant (3-mercaptopropyl) trimethoxysilane (MPTMS, 0.027 mmol neat) was added to influence the CTAB-silica micelles. The reaction was typically finished after 1 h, and the product was isolated by centrifugation and characterized.

In Qiao's method, MPTMS was proposed to insert in between CTAB molecules. It has a hydrophobic tail and a polar head (trimethoxysilane moiety). The latter can hydrolyze to become neutral or negatively charged (similar to silica). Thus, after insertion it can reduce the repulsion among the CTAB

headgroups. On the other hand, TMB has been used to expand the pore size of mesoporous silica, more specifically, for swelling the hydrophobic domains of CTAB micelles.^[27] From the point of view of packing parameters,^[25] less repulsion among the headgroups of CTAB effectively reduces the size of the hydrophilic domain, whereas swelling increases the size of the hydrophobic domain. Thus, both of these two factors favor a lower curvature of the resulting micelles (i.e., favoring lamellae or vesicles). The innovation of our method is that both MPTMS and TMB were used. The amount of TMB (TMB/CTAB up to 130) was significantly more than the typical amounts used in the literature,^[15, 28] and so was the amount of silica precursors ((TEOS+MPTMS)/CTAB = 21). As a result, CTAB played a less dominant role in the phase control, thus favoring vesicle formation.

In this same system, we prepared both cylindrical and vesicular phases of mesoporous silica by slightly varying the conditions. Without MPTMS, MCM-41 silica spheres were obtained, which were about 100 nm in overall diameter and 8 nm in pore size (Figure 2-1 a). The large pore size was a result of the swelling by TMB, consistent with similar studies using swelling agents.^[28] Depending on the orientation of the particles, the MCM-41 phase appeared as either parallel stacked cylinders or hexagonal arrays. With the inclusion of MPTMS at the onset of reaction ($t = 0$ s), silica vesicles were obtained (Figure 2-3 d), which have bilayer silica walls with uniform spacing

(14 ± 2 nm). Both the TEM contrast and the slightly crumbled appearance indicate their hollow interior. Multiple domains of a same type (MCM-41 or vesicle) were never observed in a single particle, suggesting that the phase emergence was a unified event throughout each particle.

Figure 2-1 TEM images of (a) MCM-41 silica particles obtained in the absence of MPTMS (coordinate (1.44, 0)); (b) silica particles obtained by adding MPTMS at $t = 30$ s (coordinate (1.44, 0.022)); (c) particles obtained by adding MPTMS at $t = 30$ s (coordinate (1.44, 0.027)); (d) particles obtained by adding MPTMS at $t = 60$ s (coordinate (1.44, 0.027)). Scale bars = 50nm.

Figure 2-2 Schematics illustrating the structure of silica vesicles.

The uniform spacing between the bilayer walls has a curious order that cannot be explained by random assembly. The structure must be derived from a membrane of uniform thickness, most likely that of vesicle. Previously, Wang group^[29] and Yu group^[21] reported similar structural motives, which were assigned as oxide-coated vesicles. We are inclined to a same assignment (Figure 2-2), but a potential problem is why the outer layer of silica did not hamper the formation of the inner-layer silica. If silica comes from outside of the vesicles, the difference in diffusion would at least cause dissymmetric silica walls.

Figure 2-3. (a) Phase diagram summarizing the cylinder-to-vesicle transition of mesoporous silica. TEM images of the marked points: (b) MCM-41 like cylindrical phase; (c) transition state between b and d; and (d) vesicular phase. Scale bars = 50nm.

The cylindrical and vesicular phases of mesoporous silica can be prepared under a variety of different conditions. The phase outcome was not determined by the sheer presence or absence of certain chemicals, but by the concerted effects of enough amounts of the ingredients. While excess amount of TMB can be tolerated, excess amount of MPTMS disrupted the formation of orderly phases, giving amorphous structures. By systematic control of the amount of

MPTMS and TMB, a phase diagram was prepared to illustrate the different conditions in giving the phases (Figure 2-3 a). The fact that a phase diagram can be prepared and that it is similar to the phase diagram of soft micelles^[25] suggest that the general principles of soft micelles can be applied to hard mesoporous silica, so long as the phases emerge before the hardening of silica (vide infra). We have identified 7 transition points at the boundary of cylinder-to-vesicle transition (black-yellow circles in Figure 2-3 a), where the obtained intermediates have a bilayer wall and an interior made of short and broken cylinders (Figure 2-3 c). An important characteristic of this phase diagram is that the two controlling factors were inter-dependent in phase control. For example, at coordinate (0.15, 0.027) the obtained phase is cylindrical; increasing the TMB amount to (0.86, 0.027) caused the cylinder-to-vesicle phase transition; this effects of TMB can be reversed by reducing the amount of MPTMS to (0.86, 0.016). Hence, it appears that MPTMS and TMB concertedly affect the packing parameters of the main surfactant CTAB.

Figure 2-4 Large-view TEM images of the marked point (b) in the phase diagram in **Figure 2-3a**: MCM-41 like cylindrical phase.

Figure 2-5 Large-view TEM images of the marked point (c) in the phase diagram in **Figure 2-3a**: transition state between MCM-41 like cylindrical phase and vesicular phase.

Figure 2-6 Large-view TEM images of the marked point (d) in the phase diagram in **Figure 2-3a**: vesicular phase.

Figure 2-7 Typical TEM images of the key points in the phase diagram in **Figure 2-3a**.

Figure 2-8 Phase diagram summarizing the cylinder-to-vesicle transition of mesoporous silica, with delayed addition of MPTMS at $t = 30$ s.

Careful study of the conditions showed that the phase diagram was dramatically shifted when the MPTMS addition was delayed for 30 s (the red line in Figure 2-3 a). For example, at coordinate (0.86, 0.022), the original vesicles (Figure 2-3 d) can no longer be obtained; but at (1.44, 0.027), vesicles can still form (Figure 2-1 c). When MPTMS amount was insufficient (1.44, 0.022), it converted the outmost layer to vesicles, leaving the unmodified MCM-41 phase at the center (Figure 2-1 b). Hence, it was not that the hardened silica would completely block the diffusion of MPTMS, but rather that a larger amount of it was necessary in order for enough to enter the particles. Importantly, the amount of TMB was still a key factor in the phase control, even though it was already present in the system unlike MPTMS which was

added later. In other words, a larger amount of TMB can compensate for the less amount of MPTMS diffused into the particles, highlighting the inter-dependence of the two factors.

Figure 2-9 Typical TEM images of the key points in the phase diagram in **Figure 2-8**.

2.3.2 Delayed addition of MPTMS.

When the addition of MPTMS was only slightly delayed ($t = 60$ s, coordinate (1.44, 0.027)), a same amount of it can no longer cause the same phase transition. As shown in Figure 2-1 d, MCM-41 phase was retained in most part of the particles, and only the particle surface was somewhat altered, forming a clear gap between the outmost silica layer and the MCM-41 phase. When MPTMS was added at $t = 30$ s, silica vesicles can still be obtained (Figure 2-1 c). Obviously, MPTMS must enter the particles in order to exert its effects. It should be able to diffuse into the particles at the initial stage, but the rate of diffusion was greatly reduced after 60 s. To explain the results, other ingredients except MPTMS should be already present in the initial particles at $t = 60$ s. In this set of experiments, the two types of particles should arise from the same starting particles. The fact that one type became hollow and the other did not indicated that some of the initial materials must have diffused out during the vesicle formation (*vide infra*).

Figure 2-10 Large-view TEM images of MCM-41 silica particles obtained in the absence of MPTMS (coordinate (1.44, 0)).

Figure 2-11 Nitrogen adsorption-desorption isotherm and pore size distribution of MCM-41 silica particles obtained in the absence of MPTMS (coordinate (1.44, 0))

Figure 2-12 Large-view TEM images of silica particles obtained by adding MPTMS at $t = 0$ s (MPTMS was mixed with TEOS before addition; coordinate (1.44, 0.027)).

Figure 2-13 Large view TEM images of silica particles obtained by adding MPTMS at $t = 30$ s (coordinate (1.44, 0.022)).

Figure 2-14 Large-view TEM images of silica particles obtained by adding MPTMS at $t = 30$ s (coordinate (1.44, 0.027)).

Figure 2-15 Large-view TEM images of silica particles obtained by adding MPTMS at $t = 60$ s (coordinate (1.44, 0.027)).

In a control experiment, monolayer “vesicles” were obtained by sonicating the reaction mixture (coordinate (1.44, 0.027)) at room temperature for 1 h (Figure 2-16). These hollow particles were large with a single silica wall. “Vesicles” of similar appearance have been reported previously,^[30] and they were proposed to be formed by silica deposition on surfactant-coated oil droplets. Though such “vesicles” are indeed fluid-filled sacs, they do not meet the strict definition in the micelle terminology. It appeared that sonication has promoted the segregation of ingredients,^[30-31] causing CTAB to concentrate on the surface of TMB droplets. Silica was then deposited on the droplet surface, locking the overall structure. In clear contrast, the bilayer silica vesicles should derive from a more chaotic mixture (“clumps”), where enough CTAB and silica precursor must remain inside the clumps to form the bilayer membrane and the two silica walls. Such a hypothesis is necessary to explain both the monolayer and bilayer wall structures.

Figure 2-16 Large-view TEM images of monolayer silica “vesicles” obtained by sonicating the reaction mixture at room temperature.

2.3.3 Trapping the intermediates before the formation of MCM-41 phase or silica vesicle.

To further investigate the origin of bilayer silica vesicles, we tried to trap the intermediates before their formation: After the ingredients were mixed, aliquots of solutions were extracted ($t = 10, 20, 30$, and 60 min) and directly dried on TEM sample grids. The decrease in temperature and the removal of solvent (within 2 min) helped to preserve the intermediates. Without MPTMS, the formation of MCM-41 phase can be recognized after 10 min; over time, the MCM-41 phase became clearer and so was the boundary of the particles (Figure 2-17 a-d). With MPTMS added at $t = 30$ s, the intermediates trapped at 10 min showed only spheres with solid interior (Figure 2-17 e). Over time, most of the initial materials in the particles diffused out, giving the hollow bilayer vesicles (Figure 2-17 f-h). Here, the two sets of experiments were identical except that MPTMS was added at $t = 30$ s for the second set. Hence, these particles should start from a same state, before the introduction of MPTMS diverted the CTAB-silica co-assembly to a different pathway leading to vesicles. Judging from the fact that MCM-41 phase directly emerged at 10 min^[32] and from the MPTMS diffusion experiments above, the initial “clumps” must have already taken shape at $t = 60$ s and have contained the necessary ingredients, namely CTAB, TMB and silica precursor.

Figure 2-17 TEM images of the intermediates during the formation of (a-d) MCM-41 (coordinate (1.44, 0)) and (e-h) vesicular silica particles (delayed addition of MPTMS at $t = 30$ s, coordinate (1.44, 0.027)): (a, e) 10 min; (b, f) 20 min; (c, g) 30 min; (d, h) 60 min. (i) Schematics illustrating the formation of silica vesicle from the initial clump. Scale bars = 50nm.

Thus, the first step of forming the clumps was rapid (< 60 s), and the main transformation was from large disordered assembly to ordered assembly (MCM-41 or vesicular phase). In contrast, the conventional mechanisms depict the growth from small ordered assembly to large ordered assembly. Within each individual clumps, phase emergence is also rapid (< 10 - 20 min), likely involving the “cooperative self-assembly” mechanism.

Should silica diffuse in between the surfactant micelles after their assembly, the initially formed silica layer would have hampered the later layers, causing non-uniform silica domains. Such a hypothesis is not supported by the trapped intermediates (Figure 2-17). Given the observation that the co-assembly occurred inside the clumps, it is not surprising that the silica domains in the MCM-41 and vesicular phases were highly uniform in thickness. In our recent report, we proposed that bowl-like micelles were the key intermediates in the cylinder-to-vesicle transformation of amphiphilic block copolymer micelles. In comparison, the assembly of small molecules within the clumps is much faster, preventing detailed study of the initial kinetic pathways. Here, the relatively small amount of CTAB and large amount of TMB should promote the mobility of the initial CTAB-silica assemblies, causing the phase emergence in our system to be faster than that of the traditional systems of mesoporous silica. Despite this difference, we believe that the basic principles should be generally applicable.

2.4 Conclusion

In summary, the initial mixing of CTAB, TMB, TEOS and MPTMS formed clumps, which evolved into ordered phases of MCM-41 or silica vesicles. The outcome of the self-assembly depends on the concerted effects of the ingredients as dictated by the phase diagram and the trends can be explained using packing parameters. Our system provides three new windows for inferring the complex interactions among the ingredients: (1) The inter-dependence of MPTMS and TMB in controlling the phase outcome indicates a holistic phase behavior that closely resembles that of soft micelles. (2) The altering of phase outcome by delayed addition of MPTMS (30 and 60 s) suggests that clumps of ingredients have taken shape early in the reaction and that diffusion slows down very quickly as a result of the hardening silica. (3) The temporal evolution of the clumps shows the rapid emergence of orderly phases from the disordered clumps.

In traditional studies of mesoporous silica, evidences for complex interactions among the ingredients are hard to come by. Typically, the phase outcome hinges upon a single factor (e.g., surfactant), which cannot be readily tuned. In contrast, our versatile tuning of the cylinder-to-vesicle transition reveals basic principles underlying the phase control. Such understanding permits insights in the unique behaviors of surfactant-silica co-assembly and grants readily control of the phases of mesoporous silica.

2.5 Bibliography

- [1] B. P. Mason, K. E. Price, J. L. Steinbacher, A. R. Bogdan, D. T. McQuade, *Chem. Rev.* **2007**, *107*, 2300-2318.
- [2] S. Venkataraman, J. L. Hedrick, Z. Y. Ong, C. Yang, P. L. R. Ee, P. T. Hammond, Y. Y. Yang, *Adv. Drug Deliv. Rev.* **2011**, *63*, 1228-1246.
- [3] Y.-L. Zhao, Z. Li, S. Kabehie, Y. Y. Botros, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2010**, *132*, 13016-13025.
- [4] X. Fang, X. Zhao, W. Fang, C. Chen, N. Zheng, *Nanoscale* **2013**, *5*, 2205-2218.
- [5] C. Gao, S. Che, *Adv. Funct. Mater.* **2010**, *20*, 2750-2768.
- [6] Y. Han, D. Zhang, L. L. Chng, J. Sun, L. Zhao, X. Zou, J. Y. Ying, *Nat Chem* **2009**, *1*, 123-127.
- [7] C. Wang, S. Lim, G. Du, C. Z. Loebicki, N. Li, S. Derrouiche, G. L. Haller, *J. Phys. Chem. C* **2009**, *113*, 14863-14871.
- [8] Y. Yang, G. Du, S. Lim, G. L. Haller, *Journal of Catalysis* **2005**, *234*, 318-327.
- [9] X. Lai, J. Li, B. A. Korgel, Z. Dong, Z. Li, F. Su, J. Du, D. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 2738-2741.
- [10] X. Sun, Y. Li, *Angew. Chem. Int. Ed.* **2004**, *43*, 597-601.
- [11] J. Wang, N. Yang, H. Tang, Z. Dong, Q. Jin, M. Yang, D. Kisailus, H. Zhao, Z. Tang, D. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 6417-6420.

- [12] D. E. Discher, A. Eisenberg, *Science* **2002**, 297, 967-973.
- [13] C. Liu, G. Chen, H. Sun, J. Xu, Y. Feng, Z. Zhang, T. Wu, H. Chen, *Small* **2011**, 7, 2721-2726.
- [14] Liu C. C., Yao L., Wang H., Phua Z. R., Song X. H., H. Y. Chen, Manuscript submitted.
- [15] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, *J. Am. Chem. Soc.* **1992**, 114, 10834-10843.
- [16] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem. Int. Ed.* **1999**, 38, 56-77.
- [17] D. Zhao, D. Goldfarb, *J. Chem. Soc. Chem. Commun.* **1995**, 0, 875-876.
- [18] S. S. Kim, W. Zhang, T. J. Pinnavaia, *Science* **1998**, 282, 1302-1305.
- [19] J. Liu, S. B. Hartono, Y. G. Jin, Z. Li, G. Q. Lu, S. Z. Qiao, *J. Mater. Chem.* **2010**, 20, 4595-4601.
- [20] P. T. Tanev, T. J. Pinnavaia, *Science* **1996**, 271, 1267-1269.
- [21] S. Yang, X. Zhou, P. Yuan, M. Yu, S. Xie, J. Zou, G. Q. Lu, C. Yu, *Angew. Chem. Int. Ed.* **2007**, 46, 8579-8582.
- [22] C.-Y. Chen, S. L. Burkett, H.-X. Li, M. E. Davis, *Microporous Materials* **1993**, 2, 27-34.
- [23] Y. Wan, D. Zhao, *Chem. Rev.* **2007**, 107, 2821-2860.
- [24] L. Han, K. Miyasaka, O. Terasaki, S. Che, *J. Am. Chem. Soc.* **2011**, 133,

11524-11533.

- [25] M. Antonietti, S. Förster, *Adv. Mater.* **2003**, *15*, 1323-1333.
- [26] L. Zhang, S. Qiao, Y. Jin, L. Cheng, Z. Yan, G. Q. Lu, *Adv. Funct. Mater.* **2008**, *18*, 3834-3842.
- [27] A. Fukuoka, I. Kikkawa, Y. Sasaki, A. Shimojima, T. Okubo, *Langmuir* **2009**, *25*, 10992-10997.
- [28] B. Lefèvre, A. Galarneau, J. Iapichella, C. Petitto, F. Di Renzo, F. Fajula, Z. Bayram-Hahn, R. Skudas, K. Unger, *Chem. Mater.* **2005**, *17*, 601-607.
- [29] H. Xu, W. Wang, *Angew. Chem. Int. Ed.* **2007**, *46*, 1489-1492.
- [30] S.-H. Wu, Y. Hung, C.-Y. Mou, *Chem. Mater.* **2013**, *25*, 352-364.
- [31] J.-G. Wang, F. Li, H.-J. Zhou, P.-C. Sun, D.-T. Ding, T.-H. Chen, *Chem. Mater.* **2009**, *21*, 612-620.
- [32] Y. Han, H. Yu, H. Du, W. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 1144-1150.

Chapter 3 Application: Encapsulation of Hydrophobic Fluorescent Dyes and Formation of Core-shell Nanostructures with Mesoporous Silica Shells

3.1 Introduction

Because silica NPs show less aggregation and little dye leakage than polymer-based NPs, dye-doped silica nanoparticles have a broad range of applications in tagging, tracing, and labeling.^[1-16] According to the different dye-silica interactions, there are three types of dye-doped silica nanoparticles. Firstly, dyes are attracted to the silica nanoparticles via electrostatic interaction, such as tris (2, 2'-bipyridine) ruthenium(II) chloride (Rubpy). Secondly, dyes are trapped inside the silica matrix through spatial/steric hindrance, such as tetramethylrhodamine-dextran (TMR-Dex). Thirdly, dyes can be encapsulated inside silica nanoparticles via covalent bonding: tetramethylrhodamine-5-isothiocyanate (TRITC) modified with 3-aminopropyl-triethoxysilane (APTES) to form TMR-APTES bonding to the silica nanoparticles covalently.^[17] Basically, there are two main methods for the

synthesis of dye-doped silica nanoparticles: Stöber method including some modifications of the procedure^[18] and reverse microemulsion method.^[19]

On the other hand, mesoporous silica-coated metal nanoparticles have been great studied in catalytic application.^[20-29] The precise control of the size, shape and composition of catalytic metal nanoparticles are good to the systematic investigations of the atomic-scale properties affecting catalytic activity and selectivity. This is important to design high-performance catalysts in terms of activity, selectivity and resistance to deactivation. The thermal and chemical stabilities of colloidal nanoparticle catalysts are crucial to catalytic performance. Mesoporous silica shell of the silica-coated metal nanoparticles can prevent the aggregation of metal nanoparticles in solution. In 2009, Somorjai group reported that Pt metal core coated with a mesoporous silica shell (Pt@m-SiO₂) was a high-temperature-stable model catalytic system. The mesopores provided direct access to the Pt core even up to 750°C in air. The high thermal stability made Pt@m-SiO₂ nanoparticles as catalytically active as bare Pt metal for ethylene hydrogenation and CO oxidation.^[30] Recently, Yin group reported a soft-templated method to synthesize nano-gold (sub-5 nm)@mesoporous-silica (m-SiO₂) core-shell nanospheres with controlled size and core number by using tetradecyltrimethylammonium bromide (TTAB) as a stabilizer. The Au@m-SiO₂ core-shell nanoparticles showed great sintering-resistance at 750 °C and kept high catalytic activity for CO oxidation after the treatment.^[31]

Based on the understanding of the cylinder-to-vesicle phase transition of mesoporous silica, the complex interactions among the ingredients, and cylindrical or vesicular phase directly emerges from the “clumps” of randomly mixed surfactant, co-surfactant, and silica precursor, we try to apply in doping hydrophobic fluorescent dyes molecule in silica vesicles during the formation of random “clumps” and controlling the formation of core-shell structures of MCM-41 silica shell coating metal nanoparticles cores. We have studied silica vesicles formation by using 1,3,5-trimethylbenzene (TMB) as swelling agent previously. By dissolving the hydrophobic dyes in swelling agent TMB, we develop a new method to encapsulate hydrophobic dyes in silica vesicles. We use perylene molecule as a model dye and study the release process of loaded dye.

3.2 Materials and Methods

3.2.1 Materials

All chemical reagents were used without further purification. Tetraethyl orthosilicate (TEOS, 99.9%), (3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%), 1,3,5-Trimethylbenzene (TMB, 98%), Hexadecyltrimethylammonium bromide (CTAB, 99%) were purchased from Sigma Aldrich, Hydrogen tetrachloroaurate(III) hydrate, 99.9% (metal basis Au 49%), perylene (99%) were purchased from Alfa Aesar; Copper specimen grids (200 mesh) with

formvar/carbon support film were purchased from Electron Microscopy Sciences. Florescence spectra were collected from sample solutions in a cuvette (pathlength = 1.00 cm) on a steady-state spectrofluorometer with the excitation wavelength of 434 nm. TEM images were collected on a JEM-1400 (JEOL) Transmission Electron Microscopy operated at 100-120 kV.

3.2.2 Methods

Preparation of double layer silica vesicles. The method is based on our previous study. 4 mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2 mL water. 14 μ L NaOH water solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring (stirring speed is 750rpm). 200 μ L 1,3,5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 45 μ L tetraethoxysilane (TEOS) and 5 μ L (3-mercaptopropyl) trimethoxysilane (MPTMS) were added to the above solution together to initiate the formation of double layer silica vesicles. The mixture was reacted for 1h.

Incorporation of perylene into double layer silica vesicles. The method is based on our previous study. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2 mL water. 14 μ L NaOH water solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring (stirring speed is 750rpm). 200 μ L perylene solution in TMB (4mg/mL) was

added to the hot solution. One minute later, both 45 μ L tetraethoxysilane (TEOS) and 5 μ L (3-mercaptopropyl) trimethoxysilane (MPTMS) were added to the above solution together to initiate the formation of double layer silica vesicles. The solution was reacted for 1 h.

Incorporation of hydrophobic dyes into double layer silica vesicles (use Rhodamine B base as an example). 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14 μ L NaOH water solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring (stirring speed is 750rpm). 200 μ L Rhodamine B base solution in TMB (4mg/mL) was added to the hot solution. One minute later, both 45 μ L tetraethoxysilane (TEOS) and 5 μ L (3-mercaptopropyl)trimethoxysilane (MPTMS) were added to the above solution together to initiate the formation of double layer silica vesicles. The mixture was reacted for another 1h.

Preparation of free CTAB micelles. Different amount of CTAB (50, 100, and 250 mg) was dissolved in 1 mL water by sonication, and then aged for 1h.

Fluorescence measurements of the perylene release. The purified perylene-loaded silica vesicles were concentrated to ~10 μ L by centrifugation, and the collected solution was added to a 2 mL release media in a fluorescence cuvette (H₂O, organic solvents, or free CTAB micelles). The emission intensity at 445 nm was recorded over time. The excitation wavelength was at 434 nm; all measurements were carried out in a cuvette of 1 cm pathlength.

Preparation of core-shell mesoporous silica nanostructure (use Au NPs as core as an example). 7 μ L of 2 M aqueous NaOH solution was added to a vial containing 2 mg of CTAB (0.0055 mmol) in 1 mL water. The solution was maintained at 80°C with stirring (750 rpm) until CTAB is completely dissolved. 100 μ L of neat TMB (0.72 mmol) was dispersed in this solution, forming a milky white emulsion. After being stirred for 1 min, 50 μ L of CTAB treated Au NPs aqueous solution and 10 μ L of neat TEOS (0.044 mmol) were mixed and quickly added to the above solution. The mixture was stirred at 80°C for 1h, and the product was isolated by centrifugation and characterized.

Preparation of core-shell mesoporous silica nanostructures (other nanoparticles as cores). The procedures were the same as above, except that different nanoparticles were used as cores.

Preparation of CTAB-stabilized Au nanostructure aqueous solution.

Sodium citrate stabilized Au nanoparticles were isolated by centrifugation and incubated in CTAB aqueous solution (50 mg/mL) for 12 h at room temperature. Then, the solution was purified and re-dispersed in 50 μ L water.

Preparation of CTAB-stabilized Pd nanostructure aqueous solution.

CTAB-stabilized Pd nanostructure was synthesized directly in the CTAB aqueous solution according to a reported method.^[33] Then, the reaction solution was purified by centrifugation and re-dispersed in 50 μ L water.

Preparation of CTAB-stabilized Fe₃O₄ nanostructure aqueous solution.

According to a reported method,^[32] citric acid (100 mg) was first weighed into a vial followed by the addition of DMF (1 mL), DCB (1 mL) and Fe₃O₄ NPs (20 µL). The resulting solution was incubated at 100 °C for 24 h. Then, the product was isolated by centrifugation and re-dispersed in 1 mL of deionized water. The Fe₃O₄ NPs aqueous solution was isolated again by centrifugation and incubated in CTAB aqueous solution (50 mg/mL) at 60 °C for 24 h. Finally, the Fe₃O₄ nanoparticles were purified by centrifugation and re-dispersed in 50 µL water.

Preparation of Au@SiO₂ core-shell nanostructure. According to our group's previous study,^[34] the synthesis was carried out following a modified Stöber method.^[35] 3 mL of 60 nm Au NPs were isolated by centrifugation and re-dispersed in 500 µL of water. The Au NPs aqueous solution was added to a vial containing 2.5 mL of 2-propanol and 20 µL of 2 mM MUA in ethanol. The solution was allowed to stir vigorously for 10 min, before 600 µL of TEOS (11.2 mM in water) and 90 µL of NH₃.H₂O were added. The mixture was stirred vigorously for 14 h. After that, the product was isolated by centrifugation and re-dispersed in 50 µL water.

3.3 Results and Discussions

3.3.1 Synthesis of Double Layer Silica Vesicles and Drug Loading

Previously, in the formation of silica vesicles, we applied TMB molecule as

swelling agent to take part in the cylinder-to-vesicle phase transition of mesoporous silica. The reaction solution is made up of water and TMB. The volume ratio of TMB/H₂O is 1/10. Because the TMB molecule is hydrophobic, hydrophobic dyes have good solubility in TMB but almost no solubility in water. Hence, it is a good way to import hydrophobic dyes molecule into the reaction solution by using hydrophobic dyes solution in TMB instead of pure TMB. The hydrophobic dyes will stay with TMB together to engage in the formation of silica vesicles. The hydrophobic dyes were physically entrapped inside the “clumps” of randomly mixed surfactant, co-surfactant, and silica precursor. In this way, we have developed a new method to dope hydrophobic dyes into silica nanostructures, such as Solvent green3, Nile red, Quinoline yellow ss, Solvent blue 5, Erythrosine B, Congo red, Sudan red G, Acridine orange base, and Rodamine B base.

In this new method to dope hydrophobic dyes, the dye-silica interaction is non-covalent by physical trapping. When the silica nanostructures doped with hydrophobic dyes were purified by centrifugation and re-dispersed in hydrophobic solvent, the hydrophobic dyes molecule can release from inside to fresh hydrophobic solvent. The amount and speed of the release process of hydrophobic dyes depends on the solubility of the released hydrophobic dye in the fresh hydrophobic solvent. Compared to hydrophobic solvent, it is hard to release doped hydrophobic dyes from inside to the fresh water because of the

very little solubility of hydrophobic dyes in water. In the Figure 3-1, the silica nanoparticles doped with hydrophobic dyes were purified by centrifugation, re-dispersed in water, and purified again by centrifugation. Judged from the color, it is very clear that all the hydrophobic dyes molecule stay with the silica nanoparticles at the bottom of the centrifuge tube while the supernatant water phase is almost transparent. In other words, the hydrophobic dyes can be trapped successfully in the silica vesicles.

We have explored the morphology of the silica nanostructures doped with hydrophobic dyes by taking the Nile red and Rhodamine B base as examples in Figure 3-2. The silica nanostructures doped with Nile red and Rhodamine B base were purified by centrifugation, re-dispersed in water, and purified again by centrifugation. The TEM images show that both of them are still silica vesicles. The hydrophobic dyes molecule didn't change the morphology of silica vesicles just like "guest" trapped inside the silica nanostructures.

Figure 3-1 Photograph of loading different kinds of hydrophobic dyes.

Figure 3-2 (a) Photograph of loading of Nile red and Rhodamine B base; TEM images of (b) silica vesicle doped with Nile red; (c) silica vesicle doped with Rhodamine B base.

It can generate new silica nanostructures with “high density” silica layer outside and “low density” silica inside by using only half amount of CTAB

compared to the conditions of the synthesis silica vesicles. In the same way, perylene molecule was doped into the new silica nanostructures by using perylene solution in TMB instead of pure TMB in the formation reaction. The TEM image shows that the silica nanoparticles doped with perylene have “high density” silica layer outside and “low density” silica inside (Figure 3-3a). In Figure 3-3b, the silica nanostructure doped with perylene molecule was purified by centrifugation, re-dispersed in water, and purified again by centrifugation. Judged from the color, the perylene molecule stayed together with silica nanoparticles at the bottom of the centrifuge tube.

Figure 3-3 (a) TEM image of the silica nanoparticle doped with perylene by using half amount of CTAB compared to the synthesis of silica vesicle; (b) photograph of the silica nanoparticle doped with perylene molecule.

3.3.2 Study the release process of hydrophobic dyes loaded in silica vesicles.

Hydrophobic dyes can be trapped physically inside silica vesicle. It is possible for the trapped hydrophobic dyes to release from inside to outside of hydrophobic environment. In order to study the release process, we chose silica vesicle doped with perylene molecule as the model sample and free CTAB micelle solution as the outside hydrophobic environment. The silica vesicle doped with perylene molecule was purified by centrifugation and re-dispersed into the free CTAB micelle solution. The solution was incubated and the fluorescent appearance of perylene molecule was followed in kinetic model. In Figure 3-4, we can find that the intensity of the fluorescence was low at the initial. With the incubation going, the intensity of fluorescence increased from 110 to 200 gradually in 10 h.

Figure 3-4 The Fluorescence intensity trace (at 434 nm) showing the kinetics of perylene release of silica nanostructure doped with perylene molecule in free CTAB micelles solution (50 mg/mL).

3.3.3 Synthesis of core-shell nanostructures with mesoporous silica shells.

A large number of studies have been carried out to investigate the formation of MCM-41 silica nanostructures. On the other hand, the core-shell structures of mesoporous silica coating metal nanoparticles are also studied recently. As far as we known, the mesoporous silica shell in those metal NPs@mesoporous structures is not MCM-41 phase silica. Based on our previous study of cylinder-to-vesicle phase transition of mesoporous silica, we can successfully synthesize MCM-41 phase silica coating metal nanoparticles. It is new study to

take MCM-41 phase silica as shell materials.

Figure 3-5 TEM images of the Au NPs @ mesoporous silica nanostructure.

Previously, we found that the main transformation was from large disordered

assembly to ordered assembly in the CTAB-silica co-assembly process to get MCM-41 or silica vesicle. The initial mixing of CTAB, TMB, TEOS and MPTMS formed “clumps”-the large disordered assembly. The clumps slowly evolved into ordered MCM-41 or silica vesicles. The exact pathway of the self-assembly inside the clumps depends on the concerted effects of the ingredients. By understanding the inter-dependence of MPTMS and TMB in controlling the phase outcome, we can drive the clumps to evolve into ordered MCM-41.

The method to get MCM-41 silica coating metal nanoparticles is to dope the metal nanoparticles into the initial mixing of “clumps”, and to drive the “clumps” to evolve into ordered MCM-41. In order to make sure the formation of initial clumps with the addition of metal nanoparticles, it is necessary to encapsulate the metal nanoparticles with CTAB molecule first. In Figure 3-5, the Au NPs was synthesized in CTAB aqueous solution first and doped into mixing of CTAB, TMB and TEOS at the right time. The mixture was reacted at 80°C for 1h. The TEM images show the core-shell nanostructures with either parallel-stacked cylinders or hexagonal arrays of silica shell. We have successfully synthesized core-shell AuNPs@mesoporous silica nanostructures.

In the similar way, Pd NPs, Au@Ag NPs, and Fe₃O₄ NPs were encapsulated with CTAB molecule first and doped into the initial mixing of CTAB, TMB and TEOS at right time. The initial mixture evolved to get Pd@MCM-41 (Figure

3-6), Au@Ag@MCM-41 (Figure 3-7), and Fe₃O₄@MCM-41 (Figure 3-8).

Figure 3-6 TEM images of Pd@MCM-41 silica nanostructure.

Figure 3-7 TEM images of Au@Ag@MCM-41 silica nanostructure.

Figure 3-8 TEM images of Fe₃O₄@MCM-41 silica nanostructure.

3.3.4 Synthesis the chain of Fe₃O₄@mesoporous silica nanostructures.

Recently, our group reported a simple and scalable method for fabricating

magnetic stir bars.^[32] They were straight single-line chains assembled from 40 nm Fe_3O_4 NPs and then preserved in silica shells of variable thickness. To develop the magnetic stir bars, we try to encapsulate the chains with mesoporous silica shell.

In the Figure 3-9, the straight single-line chains assembled from Fe_3O_4 NPs with thin silica shell were doped into initial mixing of CTAB-silica co-assembly at 60°C under magnetic forces. The TEM images show that it is prior to get mesoporous silica nanoparticles attached on the single-line chains than the uniform mesoporous silica shell. In the Figure 3-10, the Fe_3O_4 NPs was encapsulated with CTAB molecule and doped into initial mixing of CTAB-silica co-assembly at 60°C under magnetic forces. The TEM images show the formation of large bundle of chains assembled from Fe_3O_4 NPs and preserved in silica shells.

Figure 3-9 TEM images of the chain of Fe₃O₄ NPs with thin silica shell encapsulated with mesoporous silica.

Figure 3-10 TEM images of Fe₃O₄ NPs encapsulated with mesoporous silica under magnetic forces.

3.3.5 Synthesis of new silica nanoparticles with ordered nanochannels by doping stearic acid molecule with CTAB

Because stearic acid molecule under NaOH aqueous solution is negative charge, it is possible to be attracted to cationic CTAB molecule via electrostatic interaction. As a result, the parking of the surfactant will change to produce new template and the surfactant-silica co-assembly will generate new silica nanoparticles. According to the strategy, we design to dope stearic acid molecule into the initial mixing of CTAB, TMB, TEOS and MPTMS. In the Figure 3-11, the TEM images show the new silica nanoparticles with ordered nanochannels. We proposed that the stearic acid molecule changed the parking model of CTAB molecule in the system. In the Figure 3-12, the stearic acid molecule was also doped into the initial mixing of CTAB, TMB, TEOS and MPTMS by using half amount of TMB compared to the condition of Figure 3-11. The TEM images (Figure 3-12) show the new silica nanoparticles with perpendicular channels and thick silica shells.

Figure 3-11 TEM images of silica nanoparticles with ordered channels by doping stearic acid molecule with CTAB.

Figure 3-12 TEM images of silica nanoparticles with perpendicular channels and thick silica shells.

3.4 Conclusion

We have developed a new method to dope hydrophobic dyes into silica nanostructures by using TMB solution dissolved with hydrophobic dyes instead of pure TMB in the formation of silica vesicles. The hydrophobic dyes can be trapped successfully without change the morphology of silica vesicles. We also studied the slowly release process of perylene molecule from inside silica nanostructures to empty CTAB micelle solution.

On the other hand, by understanding the inter-dependence of MPTMS and TMB in controlling the phase outcome, we have droved the clumps to evolve into ordered MCM-41 to synthesize Au@MCM-41, Pd@MCM-41, Au@Ag@MCM-41, and Fe₃O₄@MCM-41. The large bundle of chains assembled from Fe₃O₄ NPs and preserved in silica shells was formed. In addition, new silica nanoparticles with ordered channels were found by doping stearic acid molecule with CTAB in the formation of initial clumps.

3.5 Bibliography

- [1] J. Yan, M. C. Estévez, J. E. Smith, K. Wang, X. He, L. Wang, W. Tan, *Nano Today* **2007**, 2, 44-50.
- [2] E.-B. Cho, D. O. Volkov, I. Sokolov, *Adv. Funct. Mater.* **2011**, 21, 3129-3135.
- [3] R. M. Gaikwad, M. E. Dokukin, K. Swaminathan Iyer, C. D. Woodworth, D. O. Volkov, I. Sokolov, *Analyst* **2011**, 136, 1502-1506.
- [4] S. Iyer, C. D. Woodworth, R. M. Gaikwad, Y. Y. Kievsky, I. Sokolov, *Small* **2009**, 5, 2277-2284.
- [5] S. Palantavida, N. V. Guz, C. D. Woodworth, I. Sokolov, *Nanomedicine : nanotechnology, biology, and medicine* **2013**.
- [6] E. Y. Trofimova, S. A. Grudinkin, Y. A. Kukushkina, D. A. Kurdyukov, A. V. Medvedev, M. A. Yagovkina, V. G. Golubev, *Phys. Solid State* **2012**, 54, 1298-1305.
- [7] M. Melucci, M. Zambianchi, G. Barbarella, I. Manet, M. Montalti, S. Bonacchi, E. Rampazzo, D. C. Rambaldi, A. Zattoni, P. Reschiglian, *J. Mater. Chem.* **2010**, 20, 9903-9909.
- [8] F. Gai, T. Zhou, L. Zhang, X. Li, W. Hou, X. Yang, Y. Li, X. Zhao, D. Xu, Y. Liu, Q. Huo, *Nanoscale* **2012**, 4, 6041-6049.

- [9] J. Malinge, C. Allain, A. Brosseau, P. Audebert, *Angew. Chem. Int. Ed.* **2012**, *51*, 8534-8537.
- [10] E.-B. Cho, D. O. Volkov, I. Sokolov, *Small* **2010**, *6*, 2314-2319.
- [11] M. T. Hurley, Z. Wang, A. Mahle, D. Rabin, Q. Liu, D. S. English, M. R. Zachariah, D. Stein, P. DeShong, *Adv. Funct. Mater.* **2013**, *23*, 3335-3343.
- [12] D. Genovese, S. Bonacchi, R. Juris, M. Montalti, L. Prodi, E. Rampazzo, N. Zaccheroni, *Angew. Chem. Int. Ed.* **2013**, *52*, 5965-5968.
- [13] D. O. Volkov, E.-B. Cho, I. Sokolov, *Nanoscale* **2011**, *3*, 2036-2043.
- [14] S. Santra, P. Zhang, K. Wang, R. Tapeç, W. Tan, *Anal. Chem.* **2001**, *73*, 4988-4993.
- [15] X. He, Y. Wang, K. Wang, M. Chen, S. Chen, *Anal. Chem.* **2012**, *84*, 9056-9064.
- [16] A. A. Burns, J. Vider, H. Ow, E. Herz, O. Penate-Medina, M. Baumgart, S. M. Larson, U. Wiesner, M. Bradbury, *Nano Lett.* **2008**, *9*, 442-448.
- [17] D. Ma, A. J. Kell, S. Tan, Z. J. Jakubek, B. Simard, *J. Phys. Chem. C* **2009**, *113*, 15974-15981.
- [18] H. Ow, D. R. Larson, M. Srivastava, B. A. Baird, W. W. Webb, U. Wiesner, *Nano Lett.* **2004**, *5*, 113-117.

- [19] R. P. Bagwe, C. Yang, L. R. Hilliard, W. Tan, *Langmuir* **2004**, *20*, 8336-8342.
- [20] J. E. Lee, N. Lee, H. Kim, J. Kim, S. H. Choi, J. H. Kim, T. Kim, I. C. Song, S. P. Park, W. K. Moon, T. Hyeon, *J. Am. Chem. Soc.* **2009**, *132*, 552-557.
- [21] J. Kim, J. E. Lee, J. Lee, J. H. Yu, B. C. Kim, K. An, Y. Hwang, C.-H. Shin, J.-G. Park, J. Kim, T. Hyeon, *J. Am. Chem. Soc.* **2005**, *128*, 688-689.
- [22] Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, *J. Am. Chem. Soc.* **2007**, *130*, 28-29.
- [23] W. Zhao, J. Gu, L. Zhang, H. Chen, J. Shi, *J. Am. Chem. Soc.* **2005**, *127*, 8916-8917.
- [24] R. I. Nooney, T. Dhanasekaran, Y. Chen, R. Josephs, A. E. Ostafin, *Adv. Mater.* **2002**, *14*, 529-532.
- [25] K. J. Lin, L. J. Chen, M. R. Prasad, C. Y. Cheng, *Adv. Mater.* **2004**, *16*, 1845-1849.
- [26] S. Sadasivan, E. Dujardin, M. Li, C. J. Johnson, S. Mann, *Small* **2005**, *1*, 103-106.
- [27] P. Botella, A. Corma, M. T. Navarro, *Chem. Mater.* **2007**, *19*, 1979-1983.

- [28] I. Gorelikov, N. Matsuura, *Nano Lett.* **2007**, 8, 369-373.
- [29] M. Liong, B. France, K. A. Bradley, J. I. Zink, *Adv. Mater.* **2009**, 21, 1684-1689.
- [30] S. H. Joo, J. Y. Park, C.-K. Tsung, Y. Yamada, P. Yang, G. A. Somorjai, *Nat Mater* **2009**, 8, 126-131.
- [31] C. Wu, Z.-Y. Lim, C. Zhou, W. Guo Wang, S. Zhou, H. Yin, Y. Zhu, *Chem. Commun.* **2013**, 49, 3215-3217.
- [32] W. H. Chong, L. K. Chin, R. L. S. Tan, H. Wang, A. Q. Liu, H. Chen, *Angew. Chem. Int. Ed.* **2013**, 52, 8570-8573.
- [33] W. Niu, Z.-Y. Li, L. Shi, X. Liu, H. Li, S. Han, J. Chen, G. Xu, *Cryst. Growth Des.* **2008**, 8, 4440-4444.
- [34] Y. J. Wong, L. Zhu, W. S. Teo, Y. W. Tan, Y. Yang, C. Wang, H. Chen, *J. Am. Chem. Soc.* **2011**, 133, 11422-11425.
- [35] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, 26, 62-69.

Chapter 4 Understanding and Application of Dissolution Re-growth Process during Silica Vesicles Formation

4.1 Introduction

The chemistry of silica in aqueous solution maintains as activated research topic over a centenary, which have been explored in absorption, separation, catalyst, and drug delivery.^[1-7] It is still challenge to study the dissolution and growth of silica because of the existence of a large number of silicate species and their rich chemical interactions.^[8] Understanding the dissolution and re-growth process in aqueous solution provide a window to insight the basic chemistry of silica. It is possible to control the nucleation and growth, and subsequently the crystal size and shape, of zeolite materials via systematic investigation of the dissolution and formation of silica nanoparticles.^[9-11] As a result, functional and complex silica nanostructures can be synthesized, such as hollow silica nanostructures.^[12-23]

In the past decade, hollow silica nanostructures have been extensively explored. The development of synthetic strategies included hard/soft-templating methods,^[24-29] self-templating methods,^[8] ship-in-bottle techniques,^[30] and

selective etching.^[31-33]

Recently, Yin group reported that amorphous silica colloids, when dispersed in an aqueous solution of NaBH_4 , undergo a spontaneous morphology change from solid to hollow spheres. Concurrent but separate core-dissolution and shell-growth processes were regarded as the driving force to the hollow silica structures.^[8] In another case, Zheng group reported that hollow structures with ordered mesoporous aluminosilica shells could be prepared by using silica spheres as the silica precursors treated with a hot alkaline solution in the presence of sodium aluminate and CTAB. The hollow mesoporous aluminosilica spheres with perpendicular pore channels were proposed to form by etching followed by co-assembly.^[34] It also concerned the dissolution and re-growth process of silica in the formation of hollow nanostructures.

Previously, we studied the cylinder-to-vesicle phase transition of mesoporous silica. During the study, we find that the “clumps” of randomly mixed surfactant, co-surfactant, and silica precursor that are formed at the very beginning of the reaction can convert to final hollow silica nanostructures. There is also dissolution and re-growth process during the formation of silica vesicles. And it is simply operated and controllable. Hence, if we can introduce some functional factor such as metal species, at the middle point of dissolution re-growth process, it is possible to produce many functional complex silica nanoparticles. It can provide opportunities for the development of materials

with new structures and functionalities.

4.2 Materials and Methods

4.2.1 Materials

All chemical reagents were used without further purification. Tetraethyl orthosilicate (TEOS, 99.9%), (3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%), 1,3,5-Trimethylbenzene (TMB, 98%), Hexadecyltrimethylammonium bromide (CTAB, 99%), (3-Aminopropyl)triethoxysilane (APTES, 99%), Rhodamine B base, [3-(2-aminoethylamino) propyl]trimethoxysilane (AAPTMS) were purchased from Sigma Aldrich, Hydrogen tetrachloroaurate(III) hydrate, 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; Copper specimen grids (200 mesh) with formvar/carbon support film were purchased from Electron Microscopy Sciences. Florescence spectra were collected from sample solutions in a cuvette (pathlength = 1.00 cm) on a steady-state spectrofluorometer with the excitation wavelength of 334 nm. Ultraviolet-visible (UV-vis) spectra were collected on a Cary 100 spectrophotometer. TEM images were collected on a JEM-1400 (JEOL) Transmission Electron Microscopy operated at 100 kV.

4.2.2 Methods

Preparation of double layer silica vesicles. The method is based on our previous study. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14 μ L NaOH water solution (2M) was added into the above solution and the temperature was rose up to 80°C under stirring (stirring speed is 750rpm). 200 μ L 1, 3, 5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 45 μ L tetraethoxysilane (TEOS) and 5 μ L (3-mercaptopropyl)trimethoxysilane (MPTMS) were added into the above solution together to initiate the formation of double layer silica vesicles. The mixture was heated for 1h.

Primary products of silica vesicles reacted with additional amount CATB.

The method is based on our previous study. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14 μ L NaOH water solution (2M) was added to the above solution and the temperature was rose up to 80°C under stirring (stirring speed is 750rpm). 200 μ L 1,3,5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 45 μ L tetraethoxysilane (TEOS) and 5 μ L (3-mercaptopropyl)trimethoxysilane (MPTMS) were added into the above solution together to initiate the formation of double layer silica vesicles. After 10, 20 or 30 min, additional 4mg of CTAB in 50 μ L water was added to the above solution. The mixture was reacted for 1 h totally.

Doping of copper ammonia complex into double layer silica vesicles. 4mg

hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14μL NaOH aqueous solution (2M) was added to the above solution and the temperature was 80°C under stirring (stirring speed is 750 rpm). 200μL 1, 3, 5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 45μL tetraethoxysilane (TEOS) and 5μL (3-mercaptopropyl) trimethoxysilane (MPTMS) were added to the above solution together into initiate the formation of double layer silica vesicles. After 10min, copper ammonia complex made from 100μL CuSO₄.5H₂O (100mM) with 30μL ammonia water. The mixture was reacted for another 1h.

Doping of aluminum into double layer silica vesicles to form aluminosilica nanostructures. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14μL NaOH water solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring (stirring speed is 750rpm). 200μL 1, 3, 5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 45μL tetraethoxysilane (TEOS) and 5μL (3-mercaptopropyl)trimethoxysilane (MPTMS) were added into the above solution together to initiate the formation of double layer silica vesicles. The mixture was reacted for 30min. The products were purified by centrifugation. The solid products were re-dispersed in CTAB aqueous solution (4mg/mL) with stirring for 30min. Then, the temperature was rose to 80°C while 200μL NaAlO₂ solution made from 100μL AlCl₃ aqueous solution (1M) with 100μL

NaOH aqueous solution (4M). The mixture reacted for another 1h.

Loading Rhodamine B base into aluminosilica nanostructures. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14μL NaOH aqueous solution (2M) was added to the above solution and the temperature was increased to 80°C under stirring (stirring speed is 750rpm). 200μL Rhodamine B base solution in TMB (4mg/mL) was added into the hot solution. One minute later, both 45μL tetraethoxysilane (TEOS) and 5μL (3-mercaptopropyl)trimethoxysilane (MPTMS) were added to the above solution together to initiate the formation of double layer silica vesicles. The mixture reacted for 30min. The products were purified by centrifugation. The solid products were re-dispersed in CTAB aqueous solution (4mg/mL) with stirring for 30min. Follow by, the temperature of above solution was increased to 80°C while 200μL NaAlO₂ solution made from 100μL AlCl₃ aqueous solution (1M) with 100μL NaOH aqueous solution (4M). The mixture reacted for another 1h.

Modify the formation of silica vesicles by using APTMS or AAPTMS instead of MPTMS. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14μL NaOH water solution (2M) was added to the above solution and the temperature was increased to 80°C under stirring (stirring speed is 750rpm). 200μL 1,3,5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 45μL tetraethoxysilane (TEOS) and

5 μ L (3-aminopropyl)trimethoxysilane (APTMS) or [3-(2-aminoethylamino) propyl] trimethoxysilane (AAPTMS) were added to the above solution together to initiate the formation of silica vesicles. After 10min, 100 μ L HAuCl₄ (10 mg/mL) was added to the above solution. After another 30 min, NaBH₄ solution was added to reduce HAuCl₄ to get very small size of gold nanoparticles. The mixture was reacted for another 1h.

Modify the formation of double layer silica vesicles and doping of gold nanoparticles into silica vesicles. 4mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 2mL water. 14 μ L NaOH water solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring (stirring speed is 750rpm). 200 μ L 1, 3, 5-Trimethylbenzene (TMB) was added to the hot solution. One minute later, both 20 μ L tetraethoxysilane (TEOS) and 20 μ L (3-aminopropyl)triethoxysilane (APTMS) were added to the above solution together to initiate the formation of silica vesicles. After 10min, 100 μ L HAuCl₄ (10 mg/mL) was added to the above solution. After another 30 min, NaBH₄ solution was added to reduce HAuCl₄ to get very small size of gold nanoparticles. The mixture was reacted for another 1h.

4.3 Results and Discussions

4.3.1 Synthesis of double layer silica vesicles and reaction with additional amount of CTAB to explore the dissolution re-growth process

Previously, we study the cylinder-to-vesicle phase transition of mesoporous silica and the inter-dependence of the controlling factors. It provides windows for inferring the complex interactions among the ingredients. Based on the previous results, we check the silica vesicles formation progress by trapping the intermediates during the reaction (delayed addition time of MPTMS at $t = 30$ s). After the ingredients such as CTAB, TMB, TEOS, and MPTMS were mixed, aliquots of solutions were extracted ($t = 10, 20, 30$, and 60 min) and directly dried on TEM sample grids. The decrease in temperature and the removal of solvent (within 2 min) helped to preserve the intermediates. In the case of delayed addition of MPTMS at $t = 30$ s, from the TEM images, we can see that there is no hollow structure inside the particles at the very beginning stage such as 10 min product (Figure 4-1 a). With the time going on, small hollow structures appeared in the nanoparticles (Figure 4-1 b). Over longer time, most of the initial materials in the particles diffused out, giving the hollow bilayer vesicles (Figure 4-1 d). To compare the initial intermediate with final product, it is highly possible to go through the process of dissolution re-growth. In another

words, it favors to change from random parking of all the reagent species to ordered silica vesicles.

On the other hand, if we only decrease the amount of CTAB to half and keep the other reagents similar as the formation of bilayer silica vesicle, it produced “single layer” silica vesicles not bilayer silica vesicle (Figure 4-2). We trapped the intermediates in this reaction at 10, 20, 30, and 60 min in the same way. The TEM images of the intermediates show the trend of silica species movement from inside dissolution to outside re-growth. It is also possible to go through the process of dissolution re-growth in the silica particles formation.

Figure 4-1 TEM images of the intermediates during the formation of vesicular silica particles (delayed addition time of MPTMS at $t = 30$ s: (a) 10 min; (b) 20 min; (c) 30 min; (d) 60 min. Scale bars = 100nm.

Figure 4-2 TEM images of the intermediates during the formation of silica vesicular particles by using half amount of CTAB compared to above conditions (delayed addition time of MPTMS at $t = 30$ s: (a) 10 min; (b) 20 min; (c) 30 min; (d) 60 min.

To further study the possibility of process of dissolution re-growth in the silica vesicle formation, we added additional amount of CTAB to trap the dissolved out silica species because of the interaction between CTAB and silica species. The experiments are below: before the final silica vesicles formation,

we added additional same amount of CTAB to take part in the reaction with silica species at different intermediate points. If we define the adding TEOS time point as $t = 0$, then we added additional same amount of CTAB at $t = 10$, 20, and 30 min. The final silica vesicle formation takes 1h. In the case of $t = 10$ min (Figure 4-2 a), we can find new kind layer of silica outside the silica particles that comes from the interaction between the additional CTAB and silica species. In the case of $t = 30$ min (Figure 4-2 c), we can also find new kind layer of silica outside the silica particles, which is thinner than the case of $t = 10$ min. Compared the results from $t = 10$, 20, and 30 min, we can observe the decrease trend of the thickness of the new kind layer of silica outside the silica particles from $t = 10$ min to $t = 30$ min. In another word, with the formation reaction of silica vesicles going, the amount of silica that can take part in the interaction with additional CTAB become less and less. It is possible that the dissolved out silica species were consumed to re-grow before the interaction with additional CTAB. So the process of dissolution re-growth is reasonable in the formation of silica vesicles.

Figure 4-2 TEM images of the primary products of vesicular silica reacted with additional amount of CTAB: (a) 10 min; (b) 20 min; and (c) 30 min primary products. Scale bars = 50nm.

4.3.2 Doping of copper-ammonia complex into silica vesicles.

According to the dissolution re-growth process in the formation of silica vesicles, we design to dope copper ammonia complex into silica vesicles to synthesize new functional nanoparticles. When the formation of silica vesicle is at primary stage ($t = 10$ min), we added certain amount of copper ammonia complex to react with the dissolved out silica species. From the TEM images (Figure 4-3), we can find that the new nanoparticles are different with the bilayer silica vesicle nanoparticles. The particles size was not uniform and the outside layer of the nanoparticles was darker because of the loading copper atoms. Meanwhile, we didn't find any another new kind of nanostructures in the reaction solution. With the copper-ammonia complex were consumed in the reaction, we believe that the copper ammonia complex had been doped into silica to get new functional nanostructures successfully.

Figure 4-3 TEM images of the copper ammonia complex doping into vesicular silica.

4.3.3 Doping of aluminum into silica vesicles to form aluminosilica nanostructures and loading Rhodamine B base into aluminosilica vesicles.

In the same way, it is possible to dope aluminum compound into silica vesicles. To modify the procedure of Zheng group, we try to prepare sodium aluminate solution by using aluminum chloride with sodium hydroxide. When we have got the primary stage product of silica vesicles ($t = 30$), we cooled down the solution and added additional same amount of CTAB under stirring for half an hour. Then, the temperature was increased to 80 °C and the prepared sodium aluminate solution was added. The mixture reacted for another 1h. The TEM images show the uniform aluminosilica vesicles (Figure 4-4). Those kinds of nanostructure have potential application in catalyst and drug delivery.

To explore the application of those aluminosilica nanostructures, we try to encapsulate Rhodamine B base into it. Rhodamine B base molecule was hydrophobic and can be dissolved in TMB very well. So we can prepare Rhodamine B base solution in TMB (4mg/mL). In the formation of aluminosilica vesicles, pure TMB was replaced by Rhodamine B base solution in TMB. Hence, when TMB was used to initiate the formation of emulsion, hydrophobic dye Rhodamine B base was induced into silica nanoparticles at the same time. In the Figure 4-5, Rhodamine B base encapsulated in silica nanoparticles were separated with water after centrifugation. It means

Rhodamine B base was maintained in the silica nanoparticles. The TEM images show the hollow vesicles nanostructures.

Figure 4-4 TEM images of the aluminum doping into vesicular silica to form aluminosilica nanostructures. Scale bars = 100nm.

Figure 4-5 TEM images of the Rhodamine B base loading into aluminosilica nanostructures. And photograph of Rhodamine B base encapsulated silica nanoparticles separated with water. Scale bars = 50nm

4.3.4 Modify the formation of silica vesicles and doping of gold nanoparticles into silica vesicles to apply in the reduction reaction.

Previously, we find that MPTMS is necessary to form silica vesicles by inserting in between CTAB molecules to reduce the charge repulsion among the CTAB headgroups. Instead of MPTMS, we try to modify the formation of silica vesicles by using similar molecules such as APTMS and AAPTMS. To maintain the conditions being similar with formation of bilayer silica vesicles, APTMS or AAPTMS instead of MPTMS can drive to synthesize different nanostructures. In the Figure 4-6 and Figure 4-7, the TEM images show the mesoporous silica nanostructures not silica vesicles.

Figure 4-6 TEM images of the silica nanoparticles synthesized by using APTMS instead of MPTMS.

Figure 4-7 TEM images of the silica nanoparticles synthesized by using AAPTMS instead of MPTMS.

In order to further study the role of APTMS in this reaction system. We adjusted the ratio between TEOS and APTMS from 9/1 to 1/1 in the reaction. From the TEM images, we can see that the silica vesicles are still observed. Because of the interaction between gold nanoparticles and APTMS functionalized nanoparticles, we design to dope small size gold nanoparticles into APTMS induced silica vesicles. In the same way, we added HAuCl_4 into the reaction solution at the primary stage of silica vesicles formation, and then added NaBH_4 to reduce HAuCl_4 to get small size gold nanoparticles doped with the wall of silica vesicles.

To test the catalyst activity of those functional nanoparticles, we chose the reduction reaction of 4-nitrophenol to 4-aminophenol as a model reaction. Under the reduce agent NaBH_4 , 4-nitrophenol was quickly reduced to 4-aminophenol. We use UV-spectrum to follow the progress of this reaction. In the UV spectrum, nitro- group appeared at about 400 nm while amino- group appeared at about 300 nm. With the reaction going, the peak at 400 nm decreased but the peak at 300 nm increased. It means 4-nitrophenol converted to 4-aminophenol. The reaction is fast and clear. It finished in 16 min.

Figure 4-8 TEM images of gold nanoparticles doping into silica vesicular.

Scale bars = 50nm.

Figure 4-9 The gold nanoparticles doped silica vesicles nanostructures using as catalyst in the reduction reaction of 4-nitrophenol to 4-aminophenol.

4.4 Conclusion

We have explored the process of silica dissolution and re-growth in the formation of silica vesicle by trapping the intermediates at $t = 10, 20, 30$, and 60 min. The similar results were observed by using half amount of CTAB compared to the synthesis of silica vesicles. When we added additional amount of CTAB at $t = 10, 20$, and 30 min, we can find the new generated silica layer outside the original silica nanoparticles. Furthermore, the thickness of the new generated silica shell decreased when the additional amount of CTAB was added later. Based on the existence of silica dissolution and re-growth in the silica vesicle formation, we doped copper-ammonia complex, aluminum, and/or Rhodamine B base into the silica vesicles to synthesize new functional silica nanostructures. On the other hand, we also modified the formation of silica vesicles by using APTMS or AAPTMS instead of MPTMS to get new silica nanostructures. In the case of using APTMS to initiate the formation of silica vesicle, HAuCl_4 molecule was doped into the silica nanoparticles and reduced by NaBH_4 to get small size Au nanoparticle doping with hollow silica nanostructures. In addition, we tested the catalyst activity of Au NPs doped hollow silica nanostructures in the reduction reaction of 4-nitrophenol converted to 4-aminophenol.

4.5 Bibliography

- [1] I. Pastoriza-Santos, J. Pérez-Juste, S. Carregal-Romero, P. Hervés, L. M. Liz-Marzán, *Chem. Asian J.* **2006**, *1*, 730-736.
- [2] F. Caruso, M. Spasova, V. Salgueiriño-Maceira, L. M. Liz-Marzán, *Adv. Mater.* **2001**, *13*, 1090-1094.
- [3] U. Jeong, Y. Wang, M. Ibisate, Y. Xia, *Adv. Funct. Mater.* **2005**, *15*, 1907-1921.
- [4] Y. Zhu, J. Shi, W. Shen, X. Dong, J. Feng, M. Ruan, Y. Li, *Angew. Chem. Int. Ed.* **2005**, *44*, 5083-5087.
- [5] W. J. Rieter, K. M. L. Taylor, W. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 9852-9853.
- [6] T. Zheng, J. Pang, G. Tan, J. He, G. L. McPherson, Y. Lu, V. T. John, J. Zhan, *Langmuir* **2007**, *23*, 5143-5147.
- [7] M. Vallet-Regí, *Chem. Eur. J.* **2006**, *12*, 5934-5943.
- [8] T. Zhang, J. Ge, Y. Hu, Q. Zhang, S. Aloni, Y. Yin, *Angew. Chem. Int. Ed.* **2008**, *47*, 5806-5811.
- [9] T. M. Davis, T. O. Drews, H. Ramanan, C. He, J. Dong, H. Schnablegger, M. A. Katsoulakis, E. Kokkoli, A. V. McCormick, R. L. Penn, M. Tsapatsis, *Nat Mater* **2006**, *5*, 400-408.
- [10] J. D. Rimer, O. Trofymuk, A. Navrotsky, R. F. Lobo, D. G. Vlachos, *Chem. Mater.* **2007**, *19*, 4189-4197.

- [11] S. Kumar, T. M. Davis, H. Ramanan, R. L. Penn, M. Tsapatsis, *J. Phys. Chem, B* **2007**, *111*, 3398-3403.
- [12] P. Mulvaney, M. Giersig, T. Ung, L. M. Liz-Marzán, *Adv. Mater.* **1997**, *9*, 570-575.
- [13] K. Kamata, Y. Lu, Y. Xia, *J. Am. Chem. Soc.* **2003**, *125*, 2384-2385.
- [14] J. Y. Kim, S. B. Yoon, J.-S. Yu, *Chem. Commun.* **2003**, 790-791.
- [15] X. W. Lou, L. A. Archer, Z. Yang, *Adv. Mater.* **2008**, *20*, 3987-4019.
- [16] Y. N. Ko, Y. C. Kang, S. B. Park, *Chem. Commun.* **2013**, *49*, 3884-3886.
- [17] X. Fang, X. Zhao, W. Fang, C. Chen, N. Zheng, *Nanoscale* **2013**, *5*, 2205-2218.
- [18] Z.-M. Cui, Z. Chen, C.-Y. Cao, L. Jiang, W.-G. Song, *Chem. Commun.* **2013**, *49*, 2332-2334.
- [19] R. Guttel, M. Paul, F. Schuth, *Catalysis Science & Technology* **2011**, *1*, 65-68.
- [20] X. Zhai, M. Yu, Z. Cheng, Z. Hou, P. a. Ma, D. Yang, X. Kang, Y. Dai, D. Wang, J. Lin, *Dalton Transactions* **2011**, *40*, 12818-12825.
- [21] Y. Hu, Q. Zhang, J. Goebel, T. Zhang, Y. Yin, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11836-11842.
- [22] J. C. Park, J. U. Bang, J. Lee, C. H. Ko, H. Song, *J. Mater. Chem.* **2010**, *20*, 1239-1246.
- [23] H. J. Hah, J. I. Um, S. H. Han, S. M. Koo, *Chem. Commun.* **2004**,

1012-1013.

- [24] P. M. Arnal, M. Comotti, F. Schüth, *Angew. Chem. Int. Ed.* **2006**, *45*, 8224-8227.
- [25] J. Lee, J. C. Park, H. Song, *Adv. Mater.* **2008**, *20*, 1523-1528.
- [26] X. Huang, C. Guo, J. Zuo, N. Zheng, G. D. Stucky, *Small* **2009**, *5*, 361-365.
- [27] J. Park, H. Song, *Nano Res.* **2011**, *4*, 33-49.
- [28] S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, *Angew. Chem. Int. Ed.* **2006**, *45*, 7063-7066.
- [29] K. M. Yeo, S. Choi, R. M. Anisur, J. Kim, I. S. Lee, *Angew. Chem. Int. Ed.* **2011**, *50*, 745-748.
- [30] S. Ding, J. S. Chen, G. Qi, X. Duan, Z. Wang, E. P. Giannelis, L. A. Archer, X. W. Lou, *J. Am. Chem. Soc.* **2010**, *133*, 21-23.
- [31] Q. Zhang, I. Lee, J. Ge, F. Zaera, Y. Yin, *Adv. Funct. Mater.* **2010**, *20*, 2201-2214.
- [32] Y. Chen, H. Chen, L. Guo, Q. He, F. Chen, J. Zhou, J. Feng, J. Shi, *ACS Nano* **2009**, *4*, 529-539.
- [33] X. Fang, C. Chen, Z. Liu, P. Liu, N. Zheng, *Nanoscale* **2011**, *3*, 1632-1639.
- [34] X. Fang, Z. Liu, M.-F. Hsieh, M. Chen, P. Liu, C. Chen, N. Zheng, *ACS*

Nano **2012**, 6, 4434-4444.

Chapter 5 Explore the Formation Process of Helical Mesoporous Silica

5.1 Introduction

Chiral supramolecule architecture derived from the self-assembly of small molecules is important for possible applications in materials science, chemical sensor, and enantioselective catalysis.^[1-18] Recently, the synthesis of helical mesoporous silica nanostructures has become a hot issue.^[19-23] However, the formation mechanisms of the chiral channels and the helical morphology are not yet fully explored.^[24]

In 2004, by using chiral anionic surfactant sodium *N*-acyl-L-alanate as template and quaternized aminosilanes as co-structure-directing agents (CSDA), Che reported the synthesis of ordered chiral mesoporous silica with a twisted hexagonal rod-like morphology. Transmission electron microscopy combined with computer simulations confirmed the presence of hexagonally ordered chiral channels of 2.2 nm diameter winding around the central axis of the rods. The formation of chiral channels was initially related to the chirality of the surfactant molecules.^[25-26] But in 2006, the similar helical mesoporous silica can also be synthesized by using achiral anionic surfactant (sodium dodecyl

sulfate) in the presence of CSDA from the same research group.^[27] It means that the inherent chirality of the template molecules was not necessary, and the formation of helical mesoporous silica nanostructures might be related to other driving forces. In 2006, Zhao group reported the synthesis of helical mesoporous silica by using achiral cationic surfactant hexadecyl trimethylammonium bromide (CTAB). The authors supposed the origin of the helical mesoporous silica to particle morphology transformation would reduce the surface free energy.^[24] In 2007, with CTAB surfactant as the structural template, tetraethoxysilane (TEOS) as the silica source, and ammonia solution as the basic medium, Ying group had also synthesized a series of helical mesoporous silica. Compared to the typical MCM-41 mesoporous silica synthesis, a much lower CTAB concentration and a higher concentrated ammonia solution were employed.^[28]

There are three main mechanisms about the formation of helical mesoporous silica: firstly, Che and Qiu proposed that the progressively staggered stacking of the surfactant molecules forced the resulting cylindrical micelles to twist into helices. The twisting of such individual cylinders was in turn the cause for the overall twisting of the mesoporous rods. Thus, when chiral surfactants were used, the twisting of the cylinders was biased towards a particular direction, leading to a non-zero ee. Secondly, Zhao and co-workers proposed that the main driving force was the minimization of the silica/solvent interfacial energy.

When a hexagonal bundle of straight cylindrical micelles was twisted into a helical bundle, the reduce of the surface to volume ratio (S/V) was estimated to be 5.2–6%. Thirdly, Han and co-workers proposed that the twisting of the cylinder bundles was driven by entropy: the depleting interaction of external species (ammonia, etc.) forced the bundles into a more compact helical configuration.

As the formation mechanism of the chiral channels and the helical morphology is still not clear, we try to explore the formation process of helical mesoporous silica and study the formation mechanism. In order to trap the intermediate of reaction, we adopt Qiao group's method to synthesize helical mesoporous silica at low temperature and without autoclave.^[29]

5.2 Materials and Methods

5.2.1 Materials

All chemical reagents were used without further purification. Tetraethyl orthosilicate (TEOS, 99.9%), (3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%), 1,3,5-Trimethylbenzene (TMB, 98%), Hexadecyltrimethylammonium bromide (CTAB, 99%) were purchased from Sigma Aldrich, Hydrogen tetrachloroaurate(III) hydrate, 99.9% (metal basis Au 49%) was purchased from Alfa Aesar; Copper specimen grids (200 mesh) with formvar/carbon support film were purchased from Electron Microscopy Sciences. TEM images were

collected on a JEM-1400 (JEOL) Transmission Electron Microscopy operated at 100 kV.

5.2.2 Methods

Preparation of the same helical MCM-41 mesoporous silica as Qiao's group result. 8mg hexadecyltrimethylammonium bromide (CTAB) was dissolved in 4mL water. 28 μ L NaOH water solution (2M) was added to the above solution and the temperature was increased to 80°C under stirring. 45 μ L tetraethoxysilane (TEOS) was added to the above solution, and 5 μ L (3-mercaptopropyl)trimethoxysilane (MPTMS) was separately added to drive the helical MCM-41 mesoporous silica formation.

Encapsulate helical mesoporous silica with another layer of silica shell. The synthesized helical mesoporous silica was purified by centrifugation and re-dispersed in 500 μ L water. The solution was added to a vial containing 2.5mL 2-propanol under stirring. 600 μ L TEOS aqueous solution (2.5 μ L pure TEOS in 1 mL water) and 90 μ L $\text{NH}_3\cdot\text{H}_2\text{O}$ were added to the above solution sequentially. The mixture was reacted for 12h.

Doping of HAuCl_4 molecule into helical mesoporous silica. 8mg CTAB was dissolved in 4mL water. 28 μ L NaOH aqueous solution (2M) was added to the above solution and the temperature was increased to 80°C under stirring. 45 μ L TEOS and 5 μ L MPTMS was added to the above solution sequentially. After 1

min, HAuCl_4 aqueous solution was added to dope into the silica nanostructure.

The mixture reacted 2 h.

Doping of copper-ammonia complex into helical mesoporous silica. 8mg

CTAB was dissolved in 4mL water. 28 μL NaOH water solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring.

45 μL TEOS and 5 μL MPTMS was added to the above solution sequentially.

After 1 min, copper-ammonia complex aqueous solution was added to dope into the silica nanostructure. The mixture was reacted for 2 h. Copper ammonia complex was prepared from 100 μL $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100mM) with 30 μL ammonia water.

Doping of hexadecylamine molecule into helical mesoporous silica. 8mg

CTAB was dissolved in 4mL water. 28 μL NaOH water solution (2M) was added to the above solution and the temperature was increased to 80°C under stirring. 45 μL TEOS and 5 μL MPTMS was added to the above solution sequentially. After 1 min, hexadecylamine in hexane solution was added to dope into the silica nanostructure. The mixture reacted for 2 h.

Doping of TMB into helical mesoporous silica. 8mg CTAB was dissolved in

4mL water. 28 μL NaOH aqueous solution (2M) was added to the above solution and the temperature was increased to 80°C under stirring. 45 μL TEOS and 5 μL MPTMS were added to the above solution sequentially. After 1 min, TMB was added to dope into the silica nanostructure. The mixture was reacted

for 2 h.

Doping of stearic acid into helical mesoporous silica. 8mg CTAB was dissolved in 4mL water. 28 μ L NaOH water solution (2M) was added into the above solution and the temperature was rose to 80°C under stirring. 45 μ L TEOS and 5 μ L MPTMS was added into the above solution sequentially. After 1 min, stearic acid solution was added to dope into the silica nanostructure. The mixture was reacted for 2 h.

Formation of large diameter of helical mesoporous silica by growing twice.

8mg CTAB was dissolved in 4mL water. 28 μ L NaOH water solution (2M) was added into the above solution and the temperature was increased to 80°C under stirring. The already synthesized helical mesoporous silica was dissolved and added into the above hot solution. After about one minute, 45 μ L TEOS and 5 μ L MPTMS was added to the solution sequentially.

Formation of large diameter of helical mesoporous silica by using APTES

in the second generation growth. 8mg CTAB was dissolved in 4mL water. 28 μ L NaOH aqueous solution (2M) was added to the above solution and the temperature was rose to 80°C under stirring. The as-synthesized helical mesoporous silica was dissolved and added to the above hot solution. After about one minute, 45 μ L TEOS and 5 μ L MPTMS was added to the solution sequentially.

5.3 Results and Discussions

5.3.1 Synthesis of primary helical MCM-41 mesoporous silica and encapsulated by second layer of silica shell.

Although there are many different ideas about the mechanism of helical mesoporous silica formation, it is still a challenge to make it clear. In our opinion, we proposed that the mechanism of helical mesoporous silica has something to do with the drying force. In order to test our proposal, we try to encapsulate the already synthesized helical mesoporous silica with second layer of silica in the solution before drying. We proposed that the second layer of silica have the ability to prohibit the twist during the drying process, so there is no helical mesoporous silica formation.

Firstly, we try to prepare helical mesoporous silica by the method developed by the Qiao group. Basically, the major point of this method is to prepare helical mesoporous silica by adjusting the ratio of MPTMS and TEOS under the surfactant of CTAB. MPTMS was proposed to insert in between CTAB molecules. At the beginning, we can successfully repeat the same results as Qiao group (Figure 5-1). The helical mesoporous silica contains the characterized fringes from (10) plane that is regularly appeared in the silica rod.

Furthermore, to get the second layer of silica nanostructures, modified Stöber method with 2-propanol/water mixtures solution was used. Our research

group has already applied Stöber method in several projects study. In this case, we try to form second layer of silica in the similar way by dissolving helical mesoporous silica primary product in the 2-propanol and water mixture solution and using ammonia as catalyst to react with TEOS. We can control the thickness of the second layer of silica shell by adjusting the amount of TEOS in the synthesis.

Figure 5-1 SEM and TEM images of the prepared helical mesoporous silica.

Figure 5-2 TEM images helical mesoporous silica with second thin layer of silica. Scale bars = 20nm.

The TEM images (Figure 5-2) show the second layer of silica shell has been successfully synthesized, but the fringes in the helicalmesoporous silica have no difference. It means that the second layer of silica we synthesized can't prohibit the formation of helical mesoporous silica. To analyst the details information, it is possible that the thickness of the second layer is still not large enough to provide strong power in prohibiting twist. Hence, we synthesized thicker silica layer by adding large amount of TEOS in the synthesis. Finally, we have got thicker second layer of silica shell than before, but it was so thick that the TEM beam can't go through the materials to get clear picture. The contrast is not good enough to provide information about the fringes in the helicalmesoporous silica. In other words, we have problem in following the relationship between the thickness of second layer silica and degree of twist.

Figure 5-3 TEM images of helical mesoporous silica with second thick layer of silica.

5.3.2 Explore the formation of helical mesoporous silica by doping metal species.

To solve the problem, another way is to dope some metal species into silica rod to affect the possibility of twist. So, the helical mesoporous silica prepared in the same way without drying process were modified by MPTMS, followed by doping HAuCl_4 into the silica nanostructures. From the TEM images (Figure 5-3), we can see the small size gold nanoparticles were doped in the silica rod. With the amount of consuming MPTMS increasing, the fringe in the silica rod is harder to observe. The change of fringe in the silica rod comes from the large difference of contrast between gold and silica. This method is also not good to follow the change of fringe in the silica nanostructures.

Figure 5-4 TEM images of the HAuCl_4 doping into helical mesoporous silica.

In the literature, it is reported that there are two types of twist with two twist axes. The primary twist axes lies outside the nanofiber, and the secondary twist

axes lies in the center of the nanofiber. When we doped Cu species into silica rod in the same method, we have got some primary twist helical mesoporous silica nanostructures (Figure 5-5).

Figure 5-5 TEM images of copper-ammonia complex doping into helical mesoporous silica.

Figure 5-6 TEM images of copper chloride doping into helical mesoporous silica.

5.3.3 To explore the formation of helical mesoporous silica by adding acid or additional amount of CTAB.

In order to explore the formation progress of helical mesoporous silica, we change our strategy to add acid or additional amount of CTAB to affect the parking of CTAB surfactant.

When the formation of helical mesoporous silica was initiated by the adding of TEOS and MPTMS, the products are still in primary stages. At this point time, acid molecule was added to modify the parking of CTAB. In order to make it clear, we define the time of adding MSPTM as $t = 0$. When we added acid HCl at $t = 1$ min, we have got short silica rod with clear fringe (Figure 5-7). We propose that the addition of acid reacted with NaOH to cease the hydrolysis of the TEOS and stop the growth of long silica rod. So, we can only get short one. In the same way, when we added additional amount of CTAB at $t=1$ min, the silica rod began to adhere to each other (Figure 5-8). The reason is that the additional amount of CTAB, which were added later, aggregated on the surface of the already produced short silica rod. Furthermore, the silica species in the solution reacted with the new CTAB to initiate the formation of adhered silica nanostructures.

Figure 5-7 TEM images of the helical mesoporous silica treated by HCl.

Figure 5-8 TEM images of the helical mesoporous silica reacted with additional amount of CTAB.

5.3.4 Explore the formation of helical mesoporous silica by doping organic molecules.

Based on the above results, we change our strategy to dope organic molecules to affect the parking of CTAB surfactant. Because the hydrophobic property of surfactant of CTAB comes from the chain of 16 carbon atoms, we chose hexadecylamine that also has the chain of 16 carbon atoms as doping agent. When the formation of helical mesoporous silica was initiated by the adding of TEOS and MPTMS, the products are still in primary stages. At this point time, hexadecylamine molecule was added to modify the parking of CTAB. In order to make it clear, we define the time of adding MSPTM as $t = 0$. When we added hexadecylamine at $t = 1$ min, we have got new nanostructures as “nanodumbbell” (Figure 5-9). We propose the mechanism of formation “nanodumbbell” as below: firstly, surfactant CTAB promoted the synthesis of short silica rod at the very primary stage. Secondly, the additional amount of hexadecylamine added later aggregated on the two ends of the short silica rod. Finally, the silica species in the solution reacted with amino functional group to initiate the formation of “nanodumbbell”. From those results, we have the idea that the hexadecylamine molecule has the ability to affect the parking style of CTAB. To extend the study, we design to add hexadecylamine at relatively later such as $t = 2, 5, 10$, and 30 min. The silica rod became harder and harder with the reaction going on because of the interaction between CTAB with TEOS. As

a result, it was hard for hexadecylamine to penetrate inside to take part in parking with CTAB.

Figure 5-9 TEM images of dumbbell-like silica nanostructure by doping with hexadecylamine molecule at $t = 30$ sec.

Figure 5-10 TEM images of silica nanostructure by doping with hexadecylamine molecule at $t = 2$ min.

Figure 5-11 TEM images of silica nanostructure by doping with hexadecylamine molecule at $t = 30$ min.

The TEM images (Figure 5-10) show the trend. When we added hexadecylamine at $t = 2$ min, we have got some new short silica rod with new type of fringe. It means that there is some degree of changes in the inside structures of the helical mesoporous silica. But when we added hexadecylamine at $t = 30$ min, we find the fringe in the silica rod almost keep the same as the case of without hexadecylamine (Figure 5-11). According to our proposal, if hexadecylamine molecule has chance to dope with CTAB in the packing process, the outcome of nanostructures will be different. But the details of hexadecylamine molecule doping with CTAB is still not clear. Further study is going on.

In the same way, when the stearic acid or TMB molecules were added at $t = 1$ min, silica rods with new type fringes were produced (Figure 5-12 and Figure 5-13). The organic compounds stearic acid and TMB molecules can take part in the packing process of CTAB. Finally, the new silica nanostructures were produced with the modified template of surfactant.

Figure 5-12 TEM images of silica nanostructure by doping with stearic acid molecule.

Figure 5-13 TEM images of silica nanostructure by doping with small amount of TMB molecule.

5.3.5 Characterization of large diameter helical mesoporous silica.

Although we have got some different nanostructures from original helical mesoporous silica by doping hexadecylamine molecule, it is still not clear about the relationship between drying force and formation of helical mesoporous silica.

Tang group reported that nanofibers with a large diameter had a large twist period. Furthermore, the twist period of the fibers synthesized at higher silicate concentrations became so large that the fibers were almost straight and chirality was no longer evident. The large diameter silica rod means less twist in the drying process compared to small diameter silica rod.

It was limited in Tang group about the study of the large diameter silica rod. An ideal study is that small diameter silica rod with chiral property changed to large diameter silica rod with losing chiral property in the same system. To study the relationship between the sizes of diameter in silica rod and the chiral property of mesoporous silica, we design to synthesize large diameter silica rod by second growth using first generation's product as seeds.

Figure 5-14 TEM images of silica nanostructure from helical mesoporous silica as seed mediated second round growth.

We dissolved the first generation of helical mesoporous silica in the CTAB aqueous solution and added TESO and MPTMS. After 2 h, we have got large diameter silica rod in the style of primary twist. There is no twist along the axes in the center of the fibers. The parking of CTAB is paradise with the axes in the center of the fibers. From those results, we can find the relationship between the sizes of diameter of silica rod with chiral property of mesoporous silica. The second generation's products with large diameter of silica rod limited the twist in the primary stage. This result supports the proposal that large diameter of silica rod induce only less twist in the formation of helical mesoporous silica. It also provides the possibility to regard drying force as the major reason in the formation of helical mesoporous silica.

Figure 5-15 TEM images of silica nanostructure from helical mesoporous silica as seed mediated second round growth by using APTEM instead of MPTES.

To further explore the relationship, we using APTES instead of MPTMS to prepare the second generation of silica nanostructures. The TEM images show the larger diameter of silica rod than the case of using MPTMS. The fringe is not clear. From those results, we can see that the diameter of the silica rod determined the chiral property of mesoporous silica in some degree.

5.4 Conclusion

In summary, according Qiao group's method, we explored the formation of helical mesoporous silica by using MPTMS and TEOS as silica source with CTAB as template. To study the formation mechanism of helical mesoporous silica, we try to modify the process of formation with different approach. Firstly, we encapsulated the helical mesoporous silica with second layer of silica. There was almost no difference when the thickness of the second layer of silica was thin. And it was not clear when the thickness of the second layer of silica was too thick. Secondly, we doped HAuCl_4 , copper-ammonia complex, stearic acid molecule, TMB, and hexadecylamine molecule to get different silica nanostructure. Finally, we grew the second round of mesoporous silica by using helical mesoporous silica as seed. We also synthesized large size silica nanostructure from helical mesoporous silica as seed by using APTES instead of MPTMS.

5.5 Bibliography

- [1] A. Klug, *Angewandte Chemie International Edition in English* **1983**, 22, 565-582.
- [2] A. E. Rowan, R. J. M. Nolte, *Angew. Chem. Int. Ed.* **1998**, 37, 63-68.
- [3] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, 95, 2725-2828.
- [4] E. Yashima, K. Maeda, Y. Okamoto, *Nature* **1999**, 399, 449-451.
- [5] J. H. Georger, A. Singh, R. R. Price, J. M. Schnur, P. Yager, P. E. Schoen, *J. Am. Chem. Soc.* **1987**, 109, 6169-6175.
- [6] B. N. Thomas, C. M. Lindemann, R. C. Corcoran, C. L. Cotant, J. E. Kirsch, P. J. Persichini, *J. Am. Chem. Soc.* **2002**, 124, 1227-1233.
- [7] M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, S. Lifson, *Science* **1995**, 268, 1860-1866.
- [8] K. Tang, M. M. Green, K. S. Cheon, J. V. Selinger, B. A. Garetz, *J. Am. Chem. Soc.* **2003**, 125, 7313-7323.
- [9] S. M. Yang, I. Sokolov, N. Coombs, C. T. Kresge, G. A. Ozin, *Adv. Mater.* **1999**, 11, 1427-1431.
- [10] A. Maritan, C. Micheletti, A. Trovato, J. R. Banavar, *Nature* **2000**, 406, 287-290.

- [11] Y. Wu, G. Cheng, K. Katsov, S. W. Sides, J. Wang, J. Tang, G. H. Fredrickson, M. Moskovits, G. D. Stucky, *Nat Mater* **2004**, 3, 816-822.
- [12] T. Kunitake, *Angewandte Chemie International Edition in English* **1992**, 31, 709-726.
- [13] J. H. Fuhrhop, W. Helfrich, *Chem. Rev.* **1993**, 93, 1565-1582.
- [14] D. A. Frankel, D. F. O'Brien, *J. Am. Chem. Soc.* **1994**, 116, 10057-10069.
- [15] P. Yager, P. E. Schoen, *Molecular Crystals and Liquid Crystals* **1984**, 106, 371-381.
- [16] T. E. Gier, X. Bu, P. Feng, G. D. Stucky, *Nature* **1998**, 395, 154-157.
- [17] D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2004**, 126, 6106-6114.
- [18] Y. Xu, W. Fan, S. P. Elangovan, M. Ogura, T. Okubo, *Eur. J. Inorg. Chem.* **2004**, 4547-4549.
- [19] S. M. Yang, I. Sokolov, N. Coombs, C. T. Kresge, G. A. Ozin, *Adv. Mater.* **1999**, 11, 1427-1431.
- [20] W. J. Kim, S. M. Yang, *Adv. Mater.* **2001**, 13, 1191-1195.

- [21] Y. Yang, M. Suzuki, S. Owa, H. Shirai, K. Hanabusa, *Chem. Commun.* 2005, 4462-4464.
- [22] J. H. Jung, K. Yoshida, T. Shimizu, *Langmuir* 2002, 18, 8724-8727.
- [23] H. Jin, Z. Liu, T. Ohsuna, O. Terasaki, Y. Inoue, K. Sakamoto, T. Nakanishi, K. Ariga, S. Che, *Adv. Mater.* 2006, 18, 593-596.
- [24] S. Yang, L. Zhao, C. Yu, X. Zhou, J. Tang, P. Yuan, D. Chen, D. Zhao, *J. Am. Chem. Soc.* 2006, 128, 10460-10466.
- [25] S. Che, Z. Liu, T. Ohsuna, K. Sakamoto, O. Terasaki, T. Tatsumi, *Nature* 2004, 429, 281-284.
- [26] T. Ohsuna, Z. Liu, S. Che, O. Terasaki, *Small* 2005, 1, 233-237.
- [27] X. Wu, H. Jin, Z. Liu, T. Ohsuna, O. Terasaki, K. Sakamoto, S. Che, *Chem. Mater.* 2005, 18, 241-243.
- [28] Y. Han, L. Zhao, J. Y. Ying, *Adv. Mater.* 2007, 19, 2454-2459.
- [29] L. Zhang, S. Qiao, Y. Jin, L. Cheng, Z. Yan, G. Q. Lu, *Adv. Funct. Mater.* **2008**, 18, 3834-3842.

Chapter 6 General Study of Core-Shell silica nanostructures

6.1 Introduction

The core-shell of silica nanoparticle composites with good responsiveness of core nanoparticles and outstanding performance of silica has been continuously maintained as an activated research topic, which is currently being extensively explored in absorption, separation, catalyst, and targeted drug delivery.^[1-2] In the last decade, the focus on the silica coating around core nanoparticles is to investigate their optical properties,^[3-11] self-assembly for photonics,^[12-17] or surface functionalization/conjugation for surface-enhanced Raman scattering,^[18-24] phototherapy,^[25-26] or colorimetric detection.^[27-30]

The major approaches for coating silica on the surface of core nanoparticles include Stöber process and microemulsion. In 1968, Stöber and co-workers had synthesized monodisperse spherical silica nanoparticles in basic aqueous solutions by sol-gel chemistry of silicon alkoxides.^[31] Liz-Marzán group had got the seminal silica-coating of citrate-reduced gold nanoparticles by adopting the well-established Stöber method first involving the weak surface attachment with bi-functional (3-aminopropyl) trimethoxysilane in aqueous solution.^[32] It can create colloidal stable surface-protected nanoparticles by using

bi-functional molecules via strong surface-coordination or electrostatic interaction onto core nanoparticles, which is prior to silica coating. It is necessary to have reactive hydroxyl groups to facilitate the hydrolysis/condensation of tetraethyl orthosilicate for this surface-protected nanoparticles interface.^[33]

In 2008, Yin group reported the approach to get core-satellite nanocomposite catalysts protected by a porous silica shell. The typical synthesis included derivation a monolayer of the coupling agent 3-aminopropyltriethoxysilane (APTES) to the surfaces of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, adsorption citrate-stabilized Au nanoparticles onto the silica surface as the result of the strong chemical affinity between Au and primary amines, and polyvinylpyrrolidone (PVP)-protected etching technique.^[34] In the above case, citrate-stabilized Au nanoparticles was encapsulated between the first layer and second layer of silica shell depending on the assistance of coupling agent APTES. Recently, we find that cationic species can be encapsulated into silica shell without the coupling agent. It provides a solution to develop a general, facile, and scalable approach to fabricate nanocatalyst systems.

6.2 Materials and Methods

6.2.1 Materials

All chemical reagents were used without further purification. Tetraethyl

orthosilicate (TEOS, 99.9%), (3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%), and 11-mercaptopundecanoic acid (MUA) were purchased from Sigma Aldrich; Hydrogen tetrachloroaurate(III) hydrate, 99.9% (metal basis Au 49%) and sodium citrate dihydrate (99%) were purchased from Alfa Aesar; Sodium hydroxide and $\text{NH}_3\cdot\text{H}_2\text{O}$ (AR grade, 25-28% w/w) were purchased from Sinopharm.; Copper specimen grids (200 mesh) with formvar/carbon support film (TEM grids) were purchased from Electron Microscopy Sciences. Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) Transmission Electron Microscopy operated at 100 kV.

6.2.2 Methods

Standard test. We define a “standard test” in our experiments for distinguishing the stability of silica. The tested nanoparticles were isolated by centrifugation, re-dispersed in a same volume of pure water, and then incubated at 90°C for 30 min. The resulting nanoparticles were isolated by centrifugation and then characterized by TEM. The etched silica was defined as stable silica and the unetched one was defined as unstable one.

Synthesis of pure silica nanoparticles. The method is based on our group’s previous study. 15 μL tetraethoxysilane (TEOS) was added into a vial containing 2.5 mL 2-propanol and 1.1 mL D.I. water under stirring at room temperature. After the addition of 90 μL ammonia water to the above solution,

the mixture was allowed to stir for 14h at room temperature. The product was isolated by centrifugation at 14000 rpm for 15 min, and then re-dispersed in ethanol. The diameter of the silica nanoparticle is about 150 nm.

Synthesis of 60 nm Au nanoparticles. By following the previously reported citrate reduction method, Au nanoparticles (AuNPs) were synthesized using a modified method. To ensure uniformity of the AuNPs, seed mediated growth method was used. 40 nm AuNPs were first synthesized as seed solution. In each of the growth steps: boiling water (50 mL), NaOH (100 μ L, 0.165 mM), sodium citrate (500 μ L, 34.0 mM), and HAuCl₄ (500 μ L, 29.4 mM) were added in sequence to the as-synthesized seed solution (50 mL); the resulting mixture was then refluxed for 30 min. This growth step was repeated for another 11 times, obtaining 60 nm AuNPs with uniform size (total volume of about 650 mL).

Synthesis of AuNPs@SiO₂ nanoparticles by using ammonia water as catalyst. The method is based on our group's previous study by following a modified Stöber method. 3 mL of as-synthesized 60 nm AuNPs were concentrated to 20 μ L by centrifugation at 4500 rpm (1600 g) for 15 min. The concentrated AuNPs were re-dispersed in 480 μ L of water and added to a vial containing 2.5 mL of 2-propanol and 20 μ L of 2 mM MUA in ethanol. The solution was allowed to stir vigorously for 10 min, before 600 μ L of TEOS (11.2 mM in water) and 90 μ L of NH₃.H₂O were added. The mixture (total volume = 3.71 mL, $V_{2\text{-propanol}}/V_{\text{water}} = 2.1/1$) was stirred vigorously for 14 h.

After that, the product was isolated by centrifugation at 5000 rpm (2000 g) for 15 min, re-dispersed in neat ethanol, and then stored at room temperature.

Synthesis of AuNPs@SiO₂ nanoparticles using NaOH as catalyst. The method is similar with the above one. The only difference is that NaOH instead of NH₃.H₂O acts as the catalyst in the hydrolysis of TEOS.

Doping of cationic species in pure silica nanoparticles. The method is developed by using silica nanoparticles as seeds. During the formation of second silica shell, the doping of cationic species is introduced to the solution. The details are below: 1.5 mL of as-synthesized silica particles was concentrated to 10 μ L by centrifugation at 4500 rpm (1600 g) for 15 min. The concentrated silica nanoparticles were re-dispersed in 490 μ L of water and added to a vial containing 2.5 mL of 2-propanol. The solution was allowed to stir vigorously for 10 min, before 600 μ L of TEOS (11.2 mM in water) and 90 μ L of NH₃.H₂O were added. After 2 min, the doping species such as HAuCl₄, copper ammonia complex, or HRP were added into the above solution. The mixture was stirred vigorously for 14 h. After that, the product was isolated by centrifugation at 5000 rpm (2000 g) for 15 min, re-dispersed in neat ethanol, and then stored at room temperature.

Doping of Cationic Species in Au NPs@SiO₂ Nanoparticles. The method is developed by using AuNPs@SiO₂ nanoparticles as seeds. During the formation of second silica shell, the doping of cationic species is introduced to the

solution. The details are below: 3 mL of as-synthesized silica particles were concentrated to 20 μL by centrifugation at 5000 rpm (2000 g) for 15 min. The concentrated AuNPs@SiO₂ nanoparticles were re-dispersed in 480 μL of water and added to a vial containing 2.5 mL of 2-propanol. The solution was allowed to stir vigorously for 10 min, before 600 μL of TEOS (11.2 mM in water) and 90 μL of NH₃.H₂O were added. After 2 min, the doping species such as HAuCl₄, copper ammonia complex, and HRP were added to the above solution. The mixture was stirred vigorously for 14 h. After that, the product was isolated by centrifugation at 5000 rpm (2000 g) for 15 min, re-dispersed in neat ethanol, and then stored at room temperature.

Doping of Cationic Species in Fe₃O₄ NPs@SiO₂ Nanoparticles. The method is developed by using Fe₃O₄@SiO₂ nanoparticles as seed. During the formation of second silica shell, the doping of cationic species is introduced to the solution. The details are below: 3 mL of as-synthesized silica particles were concentrated to 20 μL by centrifugation at 5000 rpm (2000 g) for 15 min. The concentrated Fe₃O₄@SiO₂ nanoparticles were re-dispersed in 480 μL of water and added to a vial containing 2.5 mL of 2-propanol. The solution was allowed to stir vigorously for 10 min, before 600 μL of TEOS (11.2 mM in water) and 90 μL of NH₃.H₂O were added. After 2 min, the doping species (copper ammonia complex) was added into the above solution. The mixture was stirred vigorously for 14 h. After that, the product was isolated by centrifugation at

5000 rpm (2000 g) for 15 min, re-dispersed in neat ethanol, and then stored at room temperature.

6.3 Results and Discussions

6.3.1 The stability of silica in SiO₂ NPs and core-shell silica NPs

At first, we use pure silica NPs as starting materials to study the stability of silica. We define the standard test to check the stability of silica by etching nanoparticles in pure water for 30 min at 90°C. Based on the fact that different kind of salt has different effect on the process of silica etching, we introduce different kind of salt to the testing solution as cooperating agent during the standard test. According the much difference in size of cationic ions, we chose LiCl, NaCl, KCl, and CsCl as our cooperating agents. The TEM images (Figure 6-1) show that LiCl and NaCl can produce some small size of pores in the standard test of etching experiments; but KCl and CsCl have already broken the inner structures of silica nanoparticles to get amorphous silica nanoparticles.

Previously, our group demonstrated that the silica shell on nanoparticles formed by stöber method is inhomogeneous in nature. The outer layer of the shell is chemically more robust than the inner layer, which can be selectively etched by hot water to fabricate sophisticated yolk-shell nanostructures. To further study the inhomogeneous silica shell, we design to use different amount of NH₃.H₂O to synthesize Au NPs@SiO₂ nanoparticles and etch the synthesized

nanoparticles in standard test condition. $\text{NH}_3\cdot\text{H}_2\text{O}$ was regarded as catalyst in the hydrolysis of TEOS. The more $\text{NH}_3\cdot\text{H}_2\text{O}$ was used, the faster TEOS was hydrolyzed and silica species was nucleated. In this reaction, we have synthesized 3 kinds of Au NPs@ SiO_2 nanoparticles by using 90 μL , 180 μL , and 720 μL $\text{NH}_3\cdot\text{H}_2\text{O}$. Furthermore, to treat the 3 kinds of nanoparticles in hot water at 90°C for 50 min, we can find that the silica shell of the particles from 90 μL $\text{NH}_3\cdot\text{H}_2\text{O}$ was almost etched completely, and some part of the silica shell of the particle from 720 μL $\text{NH}_3\cdot\text{H}_2\text{O}$ was still remained. There is very small part of the silica shell of the particle from 180 μL $\text{NH}_3\cdot\text{H}_2\text{O}$ left. Hence, the trend of more amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ making more stable silica shell is clear.

Figure 6-1 TEM images of different size cationic ions' performance in the etching experiment: (a) LiCl; (b) NaCl; (c) KCl; (d) CsCl

Figure 6-2 TEM images of Au NPs@SiO₂ nanoparticles synthesized by using different amount of NH₃.H₂O (a, c, e) and nanoparticles were etched in hot water at 90°C for 50 min (b, d, f): (a, b) 90 μL NH₃.H₂O; (c, d) 180 μL NH₃.H₂O; (e, f) 720 μL NH₃.H₂O.

As we know, $\text{NH}_3\cdot\text{H}_2\text{O}$ was regarded as catalyst in hydrolysis of TEOS in the Stöber method to synthesize Au NPs@ SiO_2 nanoparticles. We try to use NaOH instead of $\text{NH}_3\cdot\text{H}_2\text{O}$ in the formation of silica nanoparticles by Stöber method. In the same standard etching experiment in hot water, the silica shell of nanoparticles synthesized by using NaOH as catalyst was etched completely. However, in the same condition, yolk-shell nanoparticles can be observed by using $\text{NH}_3\cdot\text{H}_2\text{O}$ as catalyst. In order to get yolk-shell nanoparticles in the case of using NaOH as catalyst, we only etched the Au NPs@ SiO_2 at 90°C in water for 10 min. The TEM images show the formation of yolk-shell nanoparticles by using NaOH as catalyst. From the above result, we can see that the silica shell was easier etched by using NaOH as catalyst than $\text{NH}_3\cdot\text{H}_2\text{O}$ as catalyst.

We also find out that some kind of metal cationic species have the ability to harden the silica shell formed from Stöber method. Firstly, we synthesize Au NPs@ SiO_2 nanoparticles by using NaOH as catalyst. Then, the nanoparticles was purified by centrifugation and re-dispersed in different kind of metal salts aqueous solution to incubate 12 h. After that, the nanoparticle was purified again by centrifugation and etched at 90°C in water for 10 min. The TEM images (Figure 6-3 a) show the core-shell nanostructure of AuNPs@ SiO_2 nanoparticles by using NaOH as catalyst. It can be etched to get yolk-shell nanostructure at 90°C in water for 10 min (Figure 6-3 b). Incubation in CaCl_2 or BaCl_2 aqueous solution made the silica shell be etched almost completely. On

the other hand, Incubation in FeCl_3 or CuCl_2 aqueous solution made the silica shell can't be etched at all at 90°C in water for 10 min. We also find that it is hard to etch the silica shell by incubating in HCl or HNO_3 1M aqueous solution.

In order to Figure out the hardening effect of CuCl_2 aqueous solution to the silica shell of Au NPs@ SiO_2 nanoparticle, it was incubated in different concentration of CuCl_2 aqueous solution for 12 h and etched at 90°C in water for 10 min after purification. From the TEM images (Figure 6-4), we can find the trend that the higher concentration of CuCl_2 aqueous solution made harder silica shell. In other words, the silica shell need certain amount of CuCl_2 molecule to introduce totally hardening. In the Figure 6-4 a, there are still many hollow structures produced around the surface of Au NPs. It is just like yolk-shell nanoparticles. But in the Figure 6-4 d, it is still core-shell nanoparticle by treating at high concentration of CuCl_2 aqueous solution. The silica shell was hardened by CuCl_2 molecule.

Figure 6-3 TEM images of (a) Au NPs@SiO₂ nanoparticles synthesized by using NaOH as catalyst; (b) yolk-shell nanostructure formed from particles (a) by etching at 90°C in H₂O for 10 min; (c-h) Incubation in different aqueous solution for 12 h and etching at 90°C in H₂O for 10 min after purification: (c) CaCl₂; (d) BaCl₂; (e) FeCl₃; (f) CuCl₂; (g) HNO₃; (h) HCl.

Figure 6-4 TEM images of Au NPs@SiO₂ nanoparticles (using NaOH as catalyst to synthesize) was incubated in different concentration of CuCl₂ aqueous solution firstly, then etched at 90°C for 10 min: (a) 20 mM; (b) 40 mM; (c) 80 mM; (d) 200 mM.

6.3.2 Doping of Cationic Species in Silica NPs

Based on the interaction between silica and cationic species, it is possible to dope cationic species into the silica shell during the formation of SiO₂@SiO₂ nanoparticle. The method is developed by using silica NPs as seed. During the

formation of second layer of silica shell, the cationic species is added to the solution. The cationic species were doped between the silica NPs seed and the second layer of silica shell. Firstly, we have synthesized silica NPs according to the modified Stöber method. The diameter of silica NPs is about 150 nm. The seed mediated growth process allows the growth of second layer of silica. When we doped KMnO_4 molecule in the formation of second layer silica shell of $\text{SiO}_2@ \text{SiO}_2$ nanoparticle, the TEM images (Figure 6-5) show the uniform hollow silica nanostructures. When we doped HRP molecule in the formation of second layer silica shell of $\text{SiO}_2@ \text{SiO}_2$ nanoparticle, the TEM images (Figure 6-6) show the “sunflower like” nanostructures.

Figure 6-5 TEM images of the hollow silica nanoparticles synthesized by doping KMnO_4 molecule with silica NPs.

Figure 6-6 TEM images of the $\text{SiO}_2@\text{SiO}_2$ nanostructures synthesized by doping HRP molecule with silica NPs.

6.3.3 Doping of Cationic Species in AuNPs@SiO₂ nanoparticles

In the similar way, it is possible to dope cationic species between the first layer and second layer of silica shell in the formation of AuNPs@SiO₂@SiO₂ nanostructure. This general method provides a good way to synthesize functional silica nanostructures. During the formation of the second layer of silica shell in AuNPs@SiO₂@SiO₂ nanoparticle, KMnO₄ molecule was doped to form yolk-shell like nanostructure with Au NPs inside (Figure 6-7). In the same way, HAuCl₄ molecule was doped to the silica shell of Au NPs@SiO₂@SiO₂ nanoparticle to get small size Au nanoparticle encapsulated in the silica shell (Figure 6-8). When those nanoparticles were purified by centrifugation and re-dispersed in water under 90°C for 30 min, we can get hollow functional nanostructure with large Au NPs inside and small size Au NPs encapsulated in the silica shell. The functional hollow silica nanostructure containing Au nanoparticle is potential to apply as good catalyst (Figure 6-9).

Figure 6-7 TEM images of the yolk-shell like Au NPs@SiO₂ nanoparticle synthesized by doping KMnO₄ molecule with Au NPs@SiO₂ nanoparticle.

Figure 6-8 TEM images of Au NPs@SiO₂ nanoparticle doping with HAuCl₄ molecule to get small size Au NPs encapsulated in the silica shell.

Figure 6-9 TEM images of the hollow functional nanostructure with large Au NPs inside and small size Au NPs encapsulated in the silica shell.

It is also easy to dope copper-ammonia complex in the silica shells of Au NPs@SiO₂@SiO₂ nanoparticle. The copper-ammonia complex was added to the solution after the adding of NH₃.H₂O in the formation of AuNPs@SiO₂@SiO₂ nanoparticle by using AuNPs@SiO₂ nanoparticle as seed. In the Figure 6-10, the TEM images show the copper-ammonia complex was doped between the two layers of the AuNPs@SiO₂@SiO₂ nanoparticles. It was clear to identify the two layers of silica shells in the TEM. In the Figure 6-11, the copper-ammonia complex was added to the solution for the synthesis of second layer of silica shell in AuNPs@SiO₂@SiO₂ nanoparticle. Furthermore, additional amount of NH₃.H₂O was added to the above solution to etch the new generation of silica shell. The TEM images show the yolk-shell silica nanostructures with AuNPs@SiO₂ nanoparticles as core and silica doped with copper-ammonia complex as shell. It is potential to apply those new functional silica nanostructures in catalyst, drug delivery, and separation.

Figure 6-10 TEM images of the AuNPs@SiO₂@SiO₂ nanoparticles doped with copper-ammonia complex between the two layers of silica shells.

Figure 6-11 TEM images of the yolk-shell silica nanostructures with AuNPs@SiO₂ nanoparticles as core and silica doped with copper-ammonia complex as shell.

In the Figure 6-12, by using AuNPs@SiO₂ as seed to synthesize AuNPs@SiO₂@SiO₂ nanoparticles in Stöber method, we added H₂PtCl₆ molecule to the solution after the adding of NH₃.H₂O. The TEM images show the H₂PtCl₆ molecule was doped between the two layers of the silica shells.

We also try to dope dye molecule into the silica shell of AuNPs@SiO₂@SiO₂ nanoparticles and choose Acridine orange molecule as the model. In the same way, Acridine orange molecule was added to the solution after the adding of NH₃.H₂O to synthesize AuNPs@SiO₂@SiO₂ nanoparticles by using AuNPs@SiO₂ as seed. In the Figure 6-13, the TEM images show the Acridine orange molecule was doped between the two layers of the silica shells. Drug molecule was also doped into the silica shell of silica nanostructures. In the Figure 6-14, the TEM images show the Cisplatin molecule was also doped between the two layers of the silica shells of AuNPs@SiO₂@SiO₂ nanoparticles.

In the same strategy, we try to dope HRP molecule into the silica nanostructures. In the Figure 6-15, the TEM show the HRP molecule was doped around the silica shell of AuNPs@SiO₂ with different morphology. The uniform second silica shell wasn't observed. Instead, small size silica nanoparticles doped with HRP molecule was formed and attached to the already exist first silica shell from AuNPs@SiO₂. The new generated silica nanostructures look like “nanosunflower”.

Figure 6-12 TEM images of the AuNPs@SiO₂@SiO₂ nanoparticles doped with H₂PtCl₆ molecule between the two layers of silica shells.

Figure 6-13 TEM images of the AuNPs@SiO₂@SiO₂ nanoparticles doped with Acridine orange molecule between the two layers of silica shells.

Figure 6-14 TEM images of the AuNPs@SiO₂@SiO₂ nanoparticles doped with Cisplatin molecule between the two layers of silica shells.

Figure 6-15 TEM images of the AuNPs@SiO₂@SiO₂ nanoparticles doped with HRP molecule between the two layers of silica shells.

6.3.4 Doping of Cationic Species in $\text{Fe}_3\text{O}_4\text{NPs@SiO}_2$ nanoparticles.

It is easy to separate $\text{Fe}_3\text{O}_4\text{NPs@SiO}_2$ nanoparticles from the solution by using magnetic forces. By using $\text{Fe}_3\text{O}_4\text{NPs@SiO}_2$ nanoparticles as starting materials, the synthesis of complex functional silica nanostructures is simple, facile, and recyclable. In the formation of $\text{Fe}_3\text{O}_4\text{NPs@SiO}_2\text{@SiO}_2$ nanoparticle by using $\text{Fe}_3\text{O}_4\text{NPs@SiO}_2$ nanoparticle as seed in Stöber method, HAuCl_4 molecule was added to the solution after the addition of $\text{NH}_3\cdot\text{H}_2\text{O}$. In the Figure 6-16, the TEM images show that the small size of Au NPs was located between the two layers of silica shell in the $\text{Fe}_3\text{O}_4\text{NPs@SiO}_2\text{@SiO}_2$ nanoparticles.

Figure 6-16 TEM images of $\text{Fe}_3\text{O}_4\text{NPs}@ \text{SiO}_2@ \text{SiO}_2$ nanoparticles doped with HAuCl_4 molecule between the two layers of silica shells.

6.4 Conclusion

We have explored the stability of silica shell in silica nanoparticles and AuNPs@SiO₂ nanoparticles. LiCl, NaCl, KCl, CsCl salts have different effects on the etching of silica nanoparticles. The stability of silica NPs has relationship with the species of cationic ions. In the synthesis of AuNPs@SiO₂ nanoparticles by Stöber method, the more amount of NH₃·H₂O was used, the silica shell was harder to be etched. When the AuNPs@SiO₂ nanoparticles was synthesized by using NaOH as catalyst and incubated in CuCl₂ or FeCl₃, the silica shell was very hard to be etched in hot water. In addition, the HCl and HNO₃ molecule can also harden the silica shell. But the silica shell became easy to be etched in hot water by incubating in CaCl₂ or BaCl₂. On the other hand, we successfully doped copper-ammonia complex, KMnO₄, HRP, HAuCl₄, H₂PtCl₆, Cisplatin, and Acridine orange molecule into silica NPs, AuNPs@SiO₂, or Fe₃O₄NPs@SiO₂. The cationic species were doped between the two layers of silica shells in the nanostructures of SiO₂@SiO₂, AuNPs@SiO₂@SiO₂, or Fe₃O₄NPs@SiO₂@SiO₂.

6.5 Bibliography

- [1] S. Liu, M.-Y. Han, *Chem. Asian J.* **2010**, 5, 36-45.
- [2] C. Li, C. Ma, F. Wang, Z. Xi, Z. Wang, Y. Deng, N. He, *Journal of*

Nanoscience and Nanotechnology **2012**, *12*, 2964-2972.

- [3] T. Ung, L. M. Liz-Marzán, P. Mulvaney, *J. Phys. Chem, B* **2001**, *105*, 3441-3452.
- [4] Y. Kobayashi, M. A. Correa-Duarte, L. M. Liz-Marzán, *Langmuir* **2001**, *17*, 6375-6379.
- [5] V. Salgueiriño-Maceira, F. Caruso, L. M. Liz-Marzán, *J. Phys. Chem, B* **2003**, *107*, 10990-10994.
- [6] Y. Hamanaka, K. Fukuta, A. Nakamura, L. M. Liz-Marzan, P. Mulvaney, *Appl. Phys. Lett.* **2004**, *84*, 4938-4940.
- [7] O. G. Tovmachenko, C. Graf, D. den Havel, A. van Blaaderen, H. C. Gerritsen, *Adv. Mater.* **2006**, *18*, 91-95.
- [8] M. Grzelczak, M. A. Correa-Duarte, V. Salgueiriño-Maceira, M. Giersig, R. Diaz, L. M. Liz-Marzán, *Adv. Mater.* **2006**, *18*, 415-420.
- [9] N. Liu, B. S. Prall, V. I. Klimov, *J. Am. Chem. Soc.* **2006**, *128*, 15362-15363.
- [10] J. Rodríguez-Fernández, I. Pastoriza-Santos, J. Pérez-Juste, F. J. García de Abajo, L. M. Liz-Marzán, *J. Phys. Chem. C* **2007**, *111*, 13361-13366.
- [11] K. Aslan, M. Wu, J. R. Lakowicz, C. D. Geddes, *J. Am. Chem. Soc.* **2007**, *129*, 1524-1525.
- [12] F. Caruso, M. Spasova, V. Salgueiriño-Maceira, L. M. Liz-Marzán, *Adv. Mater.* **2001**, *13*, 1090-1094.

- [13] D. Wang, V. Salgueiriño-Maceira, L. M. Liz-Marzán, F. Caruso, *Adv. Mater.* **2002**, *14*, 908-912.
- [14] F. García-Santamaría, V. Salgueiriño-Maceira, C. López, L. M. Liz-Marzán, *Langmuir* **2002**, *18*, 4519-4522.
- [15] C. Graf, A. van Blaaderen, *Langmuir* **2001**, *18*, 524-534.
- [16] M. A. Correa-Duarte, N. Sobal, L. M. Liz-Marzán, M. Giersig, *Adv. Mater.* **2004**, *16*, 2179-2184.
- [17] D. Wang, J. Li, C. T. Chan, V. Salgueiriño-Maceira, L. M. Liz-Marzán, S. Romanov, F. Caruso, *Small* **2005**, *1*, 122-130.
- [18] W. E. Doering, S. Nie, *Anal. Chem.* **2003**, *75*, 6171-6176.
- [19] S. P. Mulvaney, M. D. Musick, C. D. Keating, M. J. Natan, *Langmuir* **2003**, *19*, 4784-4790.
- [20] J.-H. Kim, J.-S. Kim, H. Choi, S.-M. Lee, B.-H. Jun, K.-N. Yu, E. Kuk, Y.-K. Kim, D. H. Jeong, M.-H. Cho, Y.-S. Lee, *Anal. Chem.* **2006**, *78*, 6967-6973.
- [21] L. O. Brown, S. K. Doorn, *Langmuir* **2008**, *24*, 2277-2280.
- [22] M. Y. Sha, H. Xu, M. J. Natan, R. Cromer, *J. Am. Chem. Soc.* **2008**, *130*, 17214-17215.
- [23] M. Roca, A. J. Haes, *J. Am. Chem. Soc.* **2008**, *130*, 14273-14279.
- [24] M. Sanles-Sobrido, W. Exner, L. Rodríguez-Lorenzo, B. Rodríguez-González, M. A. Correa-Duarte, R. A. Álvarez-Puebla, L. M.

- Liz-Marzán, *J. Am. Chem. Soc.* **2009**, *131*, 2699-2705.
- [25] C. Radloff, N. J. Halas, *Appl. Phys. Lett.* **2001**, *79*, 674-676.
- [26] S. Lal, S. E. Clare, N. J. Halas, *Acc. Chem. Res* **2008**, *41*, 1842-1851.
- [27] S. H. Liu, M. Y. Han, *Adv. Funct. Mater.* **2005**, *15*, 961-967.
- [28] S. Liu, Z. Zhang, M. Han, *Anal. Chem.* **2005**, *77*, 2595-2600.
- [29] S. Liu, Z. Zhang, Y. Wang, F. Wang, M.-Y. Han, *Talanta* **2005**, *67*, 456-461.
- [30] Y. Kobayashi, M. Horie, M. Konno, B. Rodríguez-González, L. M. Liz-Marzán, *J. Phys. Chem, B* **2003**, *107*, 7420-7425.
- [31] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62-69.
- [32] L. M. Liz-Marzán, M. Giersig, P. Mulvaney, *Langmuir* **1996**, *12*, 4329-4335.
- [33] A. F. Wallace, J. J. DeYoreo, P. M. Dove, *J. Am. Chem. Soc.* **2009**, *131*, 5244-5250.
- [34] J. Ge, Q. Zhang, T. Zhang, Y. Yin, *Angew. Chem. Int. Ed.* **2008**, *47*, 8924-8928.

Chapter 7 Summary and Outlook

7.1 Summary

Silica has advantages in chemical inertness, optical transparency, porous structure, and size-selective permeability with broad applications in catalysis, separation, sensor technologies, medical materials, bio probes, and optics. It is of great importance to build silica nanostructures with multi-functional properties. The thesis reports the research on the synthesis and application of silica nanostructures.

At first, we study the formation mechanism of the cylinder-to-vesicle phase transition of mesoporous silica. As summarized in a phase diagram, the outcome of the surfactant-silica co-assembly can be rationally controlled just like soft micelles. By trapping intermediates and studying how the hardening silica affects molecular diffusion, this new system provides windows for inferring the complex interactions among the ingredients, which are hard to study by conventional methods. The initial mixing of CTAB, TMB, TEOS and MPTMS formed clumps, which evolved into ordered phases of MCM-41 or silica vesicles. The outcome of the self-assembly depends on the concerted effects of the ingredients as dictated by the phase diagram and the trends can be

explained using packing parameters. Our system provides three new windows for inferring the complex interactions among the ingredients: (1) the inter-dependence of MPTMS and TMB in controlling the phase outcome indicates a holistic phase behavior that closely resembles that of soft micelles. (2) The altering of phase outcome by delayed addition of MPTMS (30 and 60 s) suggests that clumps of ingredients have taken shape early in the reaction and that diffusion slows down very quickly as a result of the hardening silica. (3) The temporal evolution of the clumps shows the rapid emergence of orderly phases from the disordered clumps.

In traditional studies of mesoporous silica, evidences for complex interactions among the ingredients are hard to come by. Typically, the phase outcome hinges upon a single factor (e.g., surfactant), which cannot be readily tuned. In contrast, our versatile tuning of the cylinder-to-vesicle transition reveals basic principles underlying the phase control. Such understanding permits insights in the unique behaviors of surfactant-silica co-assembly and grants readily control of the phases of mesoporous silica.

By the understanding of the cylinder-to-vesicle phase transition of mesoporous silica, we try to apply in encapsulation of hydrophobic dyes in silica vesicles and fabrication NPs @ MCM-41silica nanostructures. We have developed a new method to dope hydrophobic dyes into silica nanostructures by using TMB solution dissolved with hydrophobic dyes instead of pure TMB in

the formation of silica vesicles. The hydrophobic dyes can be trapped successfully without change of the silica vesicles morphology. We also studied the slowly release process of perylene molecule from inside silica nanostructures to “empty” CTAB micelle solution. On the other hand, by understanding the inter-dependence of MPTMS and TMB in controlling the phase outcome, we have droved the clumps to evolve into ordered MCM-41 to synthesize Au NPs @ MCM-41, Pd NPs @ MCM-41, Au @ Ag @ MCM-41, and Fe₃O₄ NPs @ MCM-41. The large bundle of chains assembled from Fe₃O₄ NPs and preserved in silica shells was formed. In addition, new silica nanoparticles with ordered channels were found by doping stearic acid molecule with CTAB in the formation of initial clumps.

After exploration the dissolution and re-growth process in the formation of silica nanostructures, we design to synthesize new silica nanostructures. The process of silica dissolution and re-growth in the formation of silica vesicle was studied by trapping the intermediates at $t = 10, 20, 30$, and 60 min. The similar results were observed by using half amount of CTAB compared to the synthesis condition of silica vesicles. When we added additional amount of CTAB at $t = 10, 20$, and 30 min, we can find the new generated silica layer outside the original silica nanoparticles. Furthermore, the thickness of the new generated silica shell decreased when the additional amount of CTAB was added later. Based on the existence of silica dissolution and re-growth in the silica vesicle

formation, we doped copper-ammonia complex, aluminum, and/or Rhodamine B base into the silica vesicles to synthesize new functional silica nanostructures. On the other hand, we also modified the formation of silica vesicles by using APTMS or AAPTMS instead of MPTMS to get new silica nanostructures. In the case of using APTMS to initiate the formation of silica vesicle, HAuCl_4 molecule was doped into the silica nanoparticles and reduced by NaBH_4 to get small size Au nanoparticle doping with hollow silica nanostructures. After that, by the reduction reaction of 4-nitrophenol to 4-aminophenol, we tested the catalyst activity of the hollow silica nanostructures doped with Au NPs.

Furthermore, we also developed the formation mechanism of helical mesoporous silica. According to Qiao group's method, we have synthesized helical mesoporous silica by using MPTMS and TEOS as silica source with CTAB as template. To study the formation mechanism of helical mesoporous silica, we try to modify the process of formation with different approach. Firstly, we encapsulated the helical mesoporous silica with second layer of silica. There was almost no difference when the thickness of the second layer of silica was thin. And it was not clear when the thickness of the second layer of silica was too thick. Secondly, we doped HAuCl_4 , copper-ammonia complex, stearic acid molecule, TMB, and hexadecylamine molecule into the formation of helical mesoporous silica to get different silica nanostructure. Finally, we grew the second generation of mesoporous silica by using helical mesoporous silica as

seed. We also synthesized large size silica nanostructure from helical mesoporous silica as seed by using APTM instead of MPTMS.

Finally, we study the stability of silica and silica nanostructures doped with cationic species. We found that the stability of silica nanoparticles had relationship with the species of cationic ions, which were added during the etching of silica nanoparticles in hot water. For example, LiCl, NaCl, KCl, CsCl salts showed different effect in the etching of silica nanoparticles in hot water. In the synthesis of AuNPs@SiO₂ nanoparticles by Stöber method, the more amount of NH₃.H₂O was used, the silica shell was harder to be etched in hot water. When the AuNPs@SiO₂ nanoparticles was synthesized by using NaOH as catalyst and incubated in CuCl₂ or FeCl₃, the silica shell was very hard to be etched in hot water. In addition, the HCl and HNO₃ molecule can also hard the silica shell. But the silica shell became easy to be etched in hot water by incubating in CaCl₂ or BaCl₂. On the other hand, we successfully doped copper-ammonia complex, KMnO₄, HRP, HAuCl₄, H₂PtCl₆, and Acridine orange molecule into silica NPs, AuNPs@SiO₂, or Fe₃O₄NPs@SiO₂. The cationic species were doped between the two layers of silica shells in the nanostructures of SiO₂@SiO₂, AuNPs@SiO₂@SiO₂, or Fe₃O₄NPs@SiO₂@SiO₂.

7.2 Outlook

Based on the understanding of evolvement from initial large disordered clumps to ordered silica nanostructures, we try to apply in encapsulation hydrophobic dyes and fabrication metal NPs @ MCM-41 silica nanostructures. Generally, we just only provide a method to synthesize complex silica nanostructures with very little application now. So, we can do much job in application of those complex silica nanostructures in the future.

1) Control the loading and release of hydrophobic dyes in the silica nanostructure. We reported that the hydrophobic dyes have been successfully physical trapped in the silica vesicles in the chapter 3. According the concept of “Nanoacceptor” from our group’s previous study, we can also develop the method to control the release of the doped hydrophobic dyes.

2) Application of metal NPs @ MCM-41 silica nanostructures in catalyst. We have developed a new method to synthesize metal NPs @ MCM-41 silica nanostructures (chapter 3). But the application of those silica nanostructures is still new. Because the core of catalytic metal nanoparticles is fixed in the center of the silica nanostructures, the new catalyst will be stabled in the reaction solution without aggregation. Furthermore, due to the parallel stacked cylinders or hexagonal arrays in the MCM-41 phase of silica shell and large size of pores produced by using TMB as swelling agent, it provides enough space for the react agents to interact with the catalytic metal nanoparticles freedom from

outside reaction solution. At the same time, it is easy for the product molecule to penetrate to the reaction solution. As a result, it is possible to maintain the catalytic activity of the metal nanoparticles without catalyst poison. In addition, it is simple to separate and recycle the catalyst of metal NPs @ MCM-41 silica nanostructures. Different catalytic reaction will be carried on by using correlated metal nanoparticles. The application window is large. On the other hand, the AuNPs@SiO₂@SiO₂ silica nanostructures with functional molecule doped between the two layers of the silica shells can convert to complex hollow silica nanostructure by selective etching. It is possible to apply it as catalyst and separation.

3) The formation mechanism of helical mesoporous silica. The formation mechanism of helical mesoporous silica is still not fully understood. Further research work need be done in the future. There is a trend that large size diameter of helical mesoporous silica rod shows small degree of twist. We can focus on the synthesis of large size diameter of helical mesoporous silica to explore the formation mechanism. We will design to show the transition from helical mesoporous silica to non-helical mesoporous silica by increasing the size of diameter of the mesoporous silica rod.

4) The synthesis of new silica nanostructures. By understanding the existence of initial mixing clumps of CTAB, TMB, MPTMS, and TEOS, the special new anionic molecule will be added and interact with cationic surfactant CTAB to

produce new template for the synthesis of new silica nanostructure. In this way, the interaction between the new added anionic molecule and CTAB molecule will drive new type of silica-surfactant co-assembly to get new silica nanostructures.

List of Publications

1. He J. T., Ji W. J., **Yao L.**, Wang Y. W., Khezri B., Webster R. D., Chen H. Y. *
Strategy for Nano-Catalysis in a Fixed-Bed System. *Adv. Mater.* 2014
accepted.
2. **Yao L.**, Liu C. C., Chong W. H., Wang H., Chen L. Y., and Chen H. Y.*,
Understanding the Phase Emergence of Mesoporous Silica. 2014,
Submitted.
3. Liu C. C., **Yao L.**, Wang H., Phua Z. R., Song X. H., and Chen H. Y.*,
Bridging the Gap in the Micellar Transformation from Cylinders to Vesicles.
Small 2014, 10, 1332.
4. Sun H., Shen X. S., **Yao L.**, Xing S. X., Wang H., Feng Y. H., and Chen H.
Y.*, Measuring the Unusually Slow Ionic Diffusion in Polyaniline via Study
of Yolk-Shell Nanostructures. *J. Am. Chem. Soc.*, **2012**, 134, 11243.
5. Chen L. Y., Wang H., Xu J., Shen X. S., **Yao L.**, Zhu L. F., Zeng Z. Y.,
Zhang H., and Chen H. Y.*, Controlling Reversible Elastic Deformation of
Carbon Nanotube Rings. *J. Am. Chem. Soc.*, **2011**, 133, 9654.
6. Feng Y. H., Wang Y., Wang H., Chen T., Tay Y. Y., **Yao L.**, Yan Q. Y., Li S.
Z., Chen, H. Y.*, Engineering “Hot” Nanoparticles for Surface-Enhanced
Raman Scattering by Embedding Reporter Molecules in Metal Layers.
Small, **2012**, 8, 1613.