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Mesoporous Silica Nanowires by Space-Confined Organic-Inorganic Hybrid Self-Assembly

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Mesoporous Silica Nanowires by Space-Confined Organic-Inorganic Hybrid Self-Assembly

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Abstract

This research focuses on the space-confined P123-silica hybrid self-assembly. Mesoporous silica nanowires with various diameters (10 – 400nm) were synthesized via sol-gel combined vapor-induced self-assembly in both AAO and EPC channels. Scanning transmission electron Microscope (STEM) was used to characterize the samples in terms of nanopore size, ordering, and orientation. The mesoporous structure of silica wires formed in EPC with diameter less than 400 nm are first reported. Substrate effect (EPC vs AAO) and processing condition effect on the morphology of the mesoporous structure of silica wires are present and discussed. The more ordered and uniform mesoporous structure is preferentially formed in narrower substrate channel confinement. A critical diameter (dc) of hard template channels is around 30-50 nm, below which the space confinement effect leads to more uniform nanostructured nanowires; above the dc, mixed mesostructure usually exist. The formation of various meso-structures of silica wires is sensitive to process conditions.
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Table of Contents

Chapter 1: Introduction and Background 1
  1.1 Self-Assembly of Block Copolymer 1
  1.1.1 Self-Assembly 1
  1.1.2 Self-Assembly of Block Copolymer 4
  1.1.3 Self-Assembly of PEO-PPO-PEO Systems 6
  1.2 Sol-Gel Method 8
  1.2.1 Hydrolysis 9
  1.2.2 Condensation 12
  1.3 Self-Assembly of Organic-Inorganic Hybrid: Porous Inorganic Network 14
  1.4 Space-Confined Organic-Inorganic Hybrid Self-Assembly 17
    1.4.1 Current Work on Space-confined EISA of Organic-Inorganic Hybrid 17
    1.4.2 Research Objectives 21

Chapter 2: Experiment 22
  2.1 Specimen Synthesis and Processing 23
    2.1.1 Materials 23
    2.1.2 Procedure 25
  2.2 Characterization Techniques 27
    2.2.1 Preparation of STEM sample 27
    2.2.2 STEM 28

Chapter 3: Nano-Scale Channel Size Effect of AAO and EPC 30
  3.1 Nano-Scale Channel Size Effect of AAO Channels 31
    3.1.1 The Silica Wires in 200 nm AAO Channels 31
    3.1.2 The Silica Wires in AAO Channels Less than 80 nm 38
  3.2 Nanoscale Channel Size Effect of EPC 42
### List of Tables and Figures

#### Chapter 1
- Figure 1.1 Characteristics of the molecular system for the success of self-assembly 4
- Figure 1.2 Schematic phase diagram of surfactant, oil and water systems 7
- Figure 1.3 Schematic of hydrolysis and condensation of silicon-alkoxide 8
- Figure 1.4 Hydrolysis reaction Mechanisms 10
- Figure 1.5 Gel times as a function of H2O/TEOS Ratio, R 11
- Figure 1.6 Condensation reaction mechanisms 12
- Figure 1.7 Schematic representation of the nanocasting concept 16
- Figure 1.8 Columnar and circular orientation meso-structure of silica wires formed in 200nm AAO channels 18
- Figure 1.9 Chiral meso-structure of silica wires formed in AAO channels by Stucky et al. 19
- Figure 1.10 Meso-structure of silica wires formed in 400nm EPC channels 20

#### Chapter 2
- Figure 2.1 The schematic of the structure of P123, (PEO)$_{20}$(PPO)$_{70}$(PEO)$_{20}$ 23
- Figure 2.2 Cross section and top view of AAO with 200nm Channels 24
- Figure 2.3 The flowchart of the experiment procedure 26
- Figure 2.4 The schematic diagram showing the concept of space-confined silica-P123 hybrid self-assembly in channels of AAO or EPC discs 26
- Figure 2.5 Schematic of Scanning Transmission Electron Microscope 29

#### Chapter 3
- Figure 3.1 Representative STEM images of silica wires formed in 200 nm AAO 32
- Figure 3.2 Schematic representation of three possibilities for 200 nm silica wires with ordered and orientated hexagonal side-view 33
- Figure 3.3 Representative STEM images of cross-sectional-view of silica wires 34
- Figure 3.4 Representative STEM images of cross-section-view of silica wires 35
- Figure 3.5 3-D schematic of circular-channels structure 36
- Figure 3.6 Representative STEM images of silica wires formed in AAO channels 39
- Figure 3.7 Representative STEM images of silica wires formed in 73 nm AAO channel 40
- Figure 3.8 Representative STEM images of silica wires formed in 35 nm AAO channels 41
- Figure 3.9 Representative STEM images of the silica wires formed in 400nm EPC 43
- Figure 3.10 Representative STEM images of the silica wires formed in 400 nm EPC: parallel packed channels 44
- Figure 3.11 Representative STEM images of silica wires formed in 200 nm EPC 45
Figure 3.12 Representative STEM images of silica wires formed in 80 nm EPC  46
Figure 3.13 Representative STEM images of silica wires formed in 10, 30 and 50 nm EPC channels  48

Chapter 4
Figure 4.1 Representative STEM image of silica wires formed in 10 nm and 50 nm EPC channels and formed in 13 nm and 55 nm AAO channels  52
Figure 4.2 Schematic explanation of the smooth wires surface (AAO) and the “pits” surface (EPC)  53
Figure 4.3 Representative STEM image of silica wires formed in 55 nm AAO channels and formed 50 nm EPC channels  56
Figure 4.4 Schematic of P123 micelle  56
Figure 4.6 Representative SEM images of the surface of AAO and EPC substrate  57

Chapter 5
Figure 5.1 Representative STEM images of the silica wires formed in 50 nm EPC when aging time was 0.03, 1.5, 3, and 48 hours  60
Figure 5.2 Representative STEM images of the silica wires formed in 200 nm EPC when aging time was 0.03, 1.5, 3, and 48 hours  61
Figure 5.3 Representative STEM image of silica wire formed in 100 nm EPC under lower VER with the lamellar disc perpendicular to the wire axis  63
Figure 5.4 Representative STEM images of silica wires formed in 200 nm AAO by 60ºC air blow dry  65
Figure 5.5 Representative STEM image of silica wires formed in 200 nm EPC at 60ºC air blow dry  66

Chapter 6
Table 6.1 The mixture ratios used in this thesis project and by G.D. Stucky et al and Z. Liang and A.S. Susha  69
Chapter One:
Introduction and Background
1.1 Self-Assembly of Block Copolymer

1.1.1 Self-Assembly

Generally, self-assembly is the spontaneous organization of materials without external intervention, instead accomplished through non-covalent interactions (hydrogen bonding, Van der Waals forces, electrostatic forces, and π-π interactions, etc.). Self-assembly processes could be found in every corner of the universe, ranging from molecules to galaxies.

A great interest is drawn to self-assembly and it is reasonable in several aspects [1, 2, 3]. First the process of order from disorder has been a great attraction for science. Second, self-assembly processes occur on all scales. On one scale, understanding self-assembly is required in order to understand this universe. On a biological scale, self-assembly is a key to understanding life. Third, self-assembly is an essential part of nanotechnology, for it is one of the few practical strategies for reducing the size of structures meanwhile keeping structures larger than molecules. What are discussed in this thesis follow this example of producing the reducing structure size materials. Finally, self-assembly has a great future in many fields such as robotics and manufacturing and more.

The most well-studied subfield of self-assembly is molecular self-assembly. Molecular self-assembly is the assembly of molecules (or parts of molecules) with no intervention from outside sources. In molecular self-assembly, the structure of the assembly is determined by
the molecular size and structure [4]. The formation of molecular crystals [5], phase-separated polymers [6], and self-assembled monolayers, SAMs [7] are all examples of molecular self-assembly.

There are five characteristics of the molecular system to determine the success of self-assembly in the system [8], as shown in Fig 1.1. First is components, a group of molecules or segments of a polymer that interact with one another. The self-assembly of a group of molecules is called intermolecular self-assembly and that of segments of a polymer is called intra-molecular self-assembly. The interaction of these molecules leads from a less ordered state to a more ordered final state. Second are interactions. Self-assembly occurs by interaction between one molecule and another; this interaction is generally weak and non-covalent (Van der Waals and Coulomb interactions, hydrophobic interactions, and hydrogen bonds). Reversibility (or adjustability) is the third characteristic. Processes in which collision between molecules leads to irreversible sticking generate an unordered structure as glass, not crystals, the ordered structure. Forth, environment of the self-assembly of molecules normally should be a solution or an interface to allow the required motion of the components. The interaction with the environment can strongly influence the course of the self-assembly. The last characteristic is mass transport and agitation. The mobility of the molecules is the basic prerequisite for self-assembly.
Figure 1.1 A) Aggregation occurs when there is a net attraction and an equilibrium separation between the components; B and C) Schematic illustration of the essential differences between irreversible aggregation and ordered self-assembly; B) Components (shown in blue) that interact with one another irreversibly form disordered glasses (shown in green); C) Components that can equilibrate, or adjust their positions once in contact, can form ordered crystals if the ordered form is the lowest-energy form (shown in red). [8]

1.1.2 Self-Assembly of Block Copolymer

Block copolymer is an ideal material in self-assembly because of the connectivity of two or more chemically dissimilar chains. Thus the block copolymer can be thought of as giant amphiphiles who possess both hydrophilic and hydrophobic nature. With the physical properties of amphiphile, block copolymer can self-assemble into ordered morphologies, such
as lamellar, hexagonal rod, and cubic in suitable solvent. In the self-assembly, block copolymer avoids direct contact between the solvent and the blocks which are insoluble and avoids unfavorable contact among the chemically dissimilar chains. The complete phase separation is prevented by the covalent linkage between the chains. For the simplest block copolymer, AB di-block copolymer, the spatially periodic domain structure with domain size and spacing typically on the 10- to 50-nanometer scale, must then minimize unfavorable interfaces and meantime avoid overstretched the polymer blocks [6].

The self-assembly of hydrophilic–hydrophobic block copolymers in the aqueous solvent can be classified in three categories by considering their hydrophilic blocks [9]: 1) the non-ionic copolymers mainly based on poly(ethylene oxide), PEO, such as poly(ethylene oxide)-poly(propylene oxide), and poly(ethylene oxide)-polystyrene di and triblock structures; 2) the anionic copolymers with poly(acrylic acid) or poly(methacrylic acid) blocks; 3) those containing blocks of cationic or cationizable monomer units, such as poly(2-vinylpyridine), poly(4-vinylpyridine), and poly(amo(meth)acrylates). The non-ionic hydrophilic–hydrophobic block copolymers not only has the advantage of adjustable water solubility with temperature, but also has the advantage to be non-toxic and non-immunogenic, which are good for biomedical applications.

In the organic solvent solution, there are two types of block copolymer self-assembly [9]: hydrophobic–hydrophilic block copolymers and hydrophobic–hydrophobic block copolymers. The self-assembly of hydrophobic–hydrophilic block copolymer in polar organic solvent
requires that at least one of the blocks is a water-soluble sequence and also soluble in polar organic liquids or mixtures of water and water miscible solvents. The PEO block of poly(ethylene oxide)- poly(propylene oxide) system is this type with PEO block soluble in non-aqueous polar solvents, such as alcohols, formamide etc. The hydrophobic–hydrophobic block copolymers, of which none of the blocks is water-soluble, self-assemble in a variety of selective solvents. T. Liu et al. [10] reported that ABA triblock copolymers could form ‘flowerlike micelles’ within a selective solvent of the B middle block.

1.1.3 Self-Assembly of PEO-PPO-PEO Systems

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), PEO-PPO-PEO, triblock copolymers, known as Pluronics (Poloxamers) or Synperonic commercially, are widely used in biomedical and pharmaceutical applications because of their very low toxicity and low immunogenicity [11]. PEO-PPO-PEO systems also show thermo-reversible gelation around body temperature and, therefore, are particularly suitable for biomedical applications such as drug delivery, gene therapy and tissue engineering [12]. The copolymer properties can be adjusted to fit different applications by changing the total molecular weight and the length ratio of relevant blocks.

Aqueous solutions of PEO-PPO-PEO systems have dramatic temperature dependence [13, 14]. At ambient pressure, below approximately 15 °C, water is a good solvent for PPO, whereas PPO show property of hydrophobicity when temperature rises. PEO is dominantly
hydrophilic within the temperature range from 0 to 100 °C. With amphiphilic characteristics, PEO-PPO-PEO triblock copolymer self-assembles into a variety of structures including spherical, cylinder, lamellar, and complex-structured fluids like the bicontinuous as shown in Figure 1.2.

The structures of the self-assembly depend on molecular architecture (as total polymerization and relative block size), thermodynamic parameters (as temperature and pressure) and solution properties (solvents and polymer concentration). By varying the PEO/PPO ratio and the molecular weight, it is possible to tailor the final properties of these systems to meet the specific application needs.

Figure 1.2 Schematic phase diagram of surfactant, oil and water systems. Outside the composition triangle, surfactant microstructures in various phases are indicated. [15]
1.2 Sol-Gel Method

The sol-gel process is the evolution of solid networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a solid network containing liquid components (gel). In the sol-gel process, the precursors for preparation of a colloid consist of a metal or metalloid element surrendered by various ligand. For example common precursors for aluminum oxide include inorganic (containing no carbon) salts such as Al(NO$_3$)$_3$ and organic compound such as Al(OC$_4$H$_9$)$_3$. The latter is an example of alkoxide, which is the class of precursors most widely used as in sol-gel research because of their ready reaction with water. The most thoroughly studied example is silicon tetraethoxide (otherwise known as tetraethoxysilane, tetraethyl orthosilicate, TEOS, or Si(OC$_2$H$_5$)$_4$).

Two kinds of reactions are used to describe the sol-gel process: hydrolysis and condensation (alcohol and water condensation). These general reactions are schematically shown in Figure 1.3.

![Figure 1.3 Schematic of hydrolysis and condensation of silicon-alkoxide.](image-url)
Because water and alkoxides are immiscible, a mutual solvent such as an alcohol is utilized [16]. With the presence of this homogenizing agent, alcohol, hydrolysis is facilitated due to the miscibility of the alkoxide and water. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. The gel is formed when the sol particles aggregate or inter-knit into a network. The process of inorganic species polymerization is divided into a set of three stages by R.K. Ilr [17], which is different from condensation of an organic polymer:

1. Polymerization of monomers to form particles;
2. Growth of particles;
3. Linking of particles into chains, then networks that extend throughout the liquid medium, thickening into a gel.

The rate of hydrolysis and condensation reactions of a particular sol-gel process are affected major by pH, temperature, catalyst nature and concentration, and H2O/Si molar ratio (R), which are discussed below:

### 1.2.1. Hydrolysis

Hydrolysis reaction occurs by the nucleophilic attack of the oxygen in the water on the silicon atom. Two mechanisms [16] were presented as acid-catalyzed and base-catalyzed mechanism, schematically shown in Figure 1.4.
Figure 1.4 Hydrolysis reaction Mechanisms: a) Acid-Catalyzed Hydrolysis; b) Base-Catalyzed Hydrolysis.

R.K. Iler [17] divides this polymerization process into three pH domains: < pH 2, pH 2-7, and > pH 7. Because the point of zero charge, where surface charge is zero, and the isoelectric point, where electrical mobility of the silica particle is zero, are in the range of pH 1-3; both the silica solubility and dissolution rate are maximized at or above pH 7 and because the silica particles are appreciably ionized above pH 7 so that particle growth occurs without aggregation or gelation [16]. R. Aeion et al. [18] reported that the rate and extent of the hydrolysis reaction was mostly influenced by the strength and concentration of the acid or base catalyst and the hydrolysis reaction is first-order reaction by strong acid catalyzed.

The hydrolysis reaction has been performed with R values, H2O/Si molar ratio, ranging from less than 1 to over 25 [16]. An increased value of R is expected to promote the hydrolysis reaction. Meanwhile higher values of R caused more complete hydrolysis of monomers.
before significant condensation occurs [16]. Differing extents of monomer hydrolysis should affect the relative rates of the alcohol- or water-producing condensation reactions: when R << 2, the alcohol producing-condensation mechanism is favored; when R >=2, the water-forming condensation reaction is favored [19].

Although an increased value of R generally promotes hydrolysis, while maintaining a constant solvent/silicate ratio, the silicate concentration is reduced when R is increased. This in turn reduces the hydrolysis and condensation rates, resulting in longer gel times, which is illuminated in Figure 1.5 showing gel times for acid-catalyzed TEOS systems as a function of R and the initial alcohol/TEOS molar ratio [20].

Besides pH, strength and concentration of acid or base catalyst, and H2O/silica precursor ratio, the rate of hydrolysis is also affected by difference of the solvent, and steric hindrance and inductive effect of the silica precursors.

Figure 1.5 Gel times as a function of H2O/ TEOS Ratio, R. [20]
1.2.2 Condensation

Two mechanisms [16] of the condensation have been presented: the acid-catalyzed and base-catalyzed mechanism, schematically shown in Figure 1.6.

Figure 1.6 Condensation reaction mechanisms: a) Acid-Catalyzed Hydrolysis; b) Base-Catalyzed Hydrolysis.

Polymerization to form siloxane bonds occurs by either an alcohol-producing or a water-producing condensation reaction. It has been shown by V.Q. Engelhardt et al. [21] that a typical sequence of condensation products is monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer, and higher order rings. The rate of these ring opening polymerizations and monomer addition reactions is dependent upon the environmental pH. In polymerizations below pH 2, the condensation rates are proportional to the [H+] concentration. Because the solubility of silica is quite low below pH 2, formation and aggregation of primary silica particles occur together and ripening (i.e., growth of a network)
contributes little to growth after particles exceed 2 nm in diameter. Thus, developing gel networks are composed of exceedingly small primary particles [16]. Between pH 2 and pH 6 condensation rates are proportional to [-OH] concentrations. The solubility of silica in this pH range is again low and particle growth stops when the particles reach 2 to 4 nm in diameter. Above pH 7, polymerization occurs the same as in the pH 2 to pH 6 range [16].

As listed in the above discussion, many factors affect the resulting silica network, such as, pH, reagent concentrations, catalyst nature and concentration, H2O/Si molar ratio (R). Generally speaking sol-gel derived silicon oxide networks, under acid-catalyzed conditions, yield primarily linear or randomly branched polymers which entangle and form additional branches resulting in gelation. On the other hand, silicon oxide networks derived under base-catalyzed conditions yield more highly branched clusters which do not interpenetrate prior to gelation and thus behave as discrete clusters [16]
1.3 Self-Assembly of Organic-Inorganic Hybrid: Porous Inorganic Network

Mesoporous nanostructures are solids with regular pore sizes ranging from 2 to 50 nm and with a narrow pore size distribution. Mesoporous solids are used technically as adsorbents, catalysts and catalyst supports owing to their high surface areas. For instance, mesoporous crystalline TiO2 could be beneficial for various applications like solar cells [22, 23] and photo-catalysis [24]. Since the discovery of MCM-41 (Mobile Crystalline Material 41) in 1992 [25], many research groups have focused their interests on mesoporous materials [26]. How to produce solids with ordered pore systems with broad dimension is of great interest.

In the past ten years appropriate amphiphilic block copolymers have been developed and used as templates to generate inorganic solids with controlled pore morphology in the nanometer scale. One mechanism was proposed as nano-casting [27, 28, 29]. The ordered structure of self-assembly of block copolymer is used as structure-directing media for the ordered mesoporous inorganic solids. The sol-gel synthesis of the inorganic nanostructure takes place in the ordered environment of a block-copolymer mesophase. The polycondensation of a water-soluble inorganic monomer is confined within the aqueous domains of a microphase separated medium, which acts as a template for the inorganic nanostructure. In another words, the self-assembly of “soft,” fragile matter is literally hard-copied into inorganic hard matter, with all the advantageous properties resulting from the inorganic world as shown in Figure 1.7. Advantages to this method include the beneficial result that the inorganic solid is a direct cast of the liquid crystalline phase formed
by block-copolymer, which indicates a high degree of control over the structure. Further, mesoporous inorganic solid prepared in liquid crystalline phases can be obtained as monoliths (large, crack-free objects, which usually are not macroscopically aligned). Through this approach, the inorganic solid are fitted out with the properties that make them valuable for different areas of materials science, e.g. chemical sensing, piezoelectricity, catalysis, solar cells, etc. However, there are still some important challenges that hinder a broader application of block copolymer templated mesostructures in technical devices [30]. For instance, although various mesostructures have been obtained as high quality thin films with thicknesses of up to several micrometers, the preparation of much thicker layers is still a problem. Such thick layers geometries are needed for various applications, for example catalytically active coatings. The nano-casting mechanism assumed that the sol-gel of the inorganic precursor would not affect or interfere the self-assembly of the organic, block copolymer. In the situation of this thesis project, the block polymer and the inorganic precursor undergo a cooperative self-assembly and is called organic-inorganic hybrid self-assembly, which means the self-assembly of the triblock copolymer interferes and even is hindered by the sol-gel of inorganic precursor.
Figure 1.7 Schematic representation of the nanocasting concept: the nanocasting involves two main steps, (a) provision of a suitable template, and (b) the casting step. Units of different dimensions and different aggregation levels can act as templates, such as molecules, aggregated structures of amphiphiles, colloids or colloidal crystals. In the casting step (b) this template unit has to be surrounded by a network-precursor small enough to be able to follow the details of the template, and its cross-linking has to preserve the original structure. The final pores are obtained by removal of the template, e.g. by calcination. [29]
1.4 Space-Confined Organic-Inorganic Hybrid Self-Assembly

1.4.1 Current Work on Space-confined EISA of Organic-Inorganic Hybrid

The ordered mesoporous silica by organic-inorganic hybrid self-assembly has a large range of application such as catalysis, adsorption, and molecular separation and as a template for producing other inorganic wires [31, 32]. The organic-inorganic hybrid self-assembly film and particles [25, 33, 34, 35, 36] has already been thoroughly investigated. In the case of thin-film, the self-assembled 2-D hexagonal channels are usually parallel to the substrate surface [37]. The organic-inorganic hybrid self-assembled nanowires within the regular larger channels (120nm~200nm) of anodized alumina oxide (AAO) were also explored [38, 39, 40, 41]. Two major nano-porous structures were reported: 1) the long axes of the mesopores aligned with the long axes of the AAO channels (columnar orientation); 2) the mesopore aligned in the axial direction (circular orientation) by changing the concentration of the surfactant [38] or silica/surfactant ratio [40] or the humidity condition of the sol-gel process [41]. These two major structures are shown in Figure 1.8 (b & d respectively).
Figure 1.8 a, b) Silica nanorods with mesopores’ channel parallel; c, d) silica nanorods with mesopores channel perpendicular to the long axes. [41]
The systematic study on the silica-P123 hybrid self-assembly in the smaller channels (<80 nm) of the AAO was reported by G. D. Stucky et al. [42]. They used a dip coating process to control the evaporation process. It’s reported that experiment and computer simulation obtained the same results. Silica mesostructures with chiral mesopores such as single and double-helical geometries formed in the channels (<80 nm) of AAO and a transition is observed in the mesopore morphology from a coiled cylindrical to a spherical cage-like geometry as shown in Figure 1.9.

Figure 1.9 Representative TEM images of mesostructures formed inside alumina nanochannels with differing confinement dimensions. The structures are a, three-layer stacked doughnuts; b, S-helix; c, core–shell D-helix, in which the core and the shell are both S-helix; d, core–shell triple-helix, in which the shell is a D-helix and the core is a S-helix; e, D-helix; f, g, S-helix with a straight core channel; h, D-helix; i, j inverted peapod structure with two lines of spherical cages packed along the long axis of the alumina nanochannel; k, l, inverted peapod with one line of cages. [42]
Z. Liang et al. [43] reported ordered mesopore structures of silica nanotubes and nanowires formed in the 400 nm track-etched polycarbonate (EPC) channels. In their studies, the EPC substrates were merged in the 3-hours-aged solution for 1.5 hours and sonication was used at the beginning of the soak to help the diffusion of solution into EPC membrane pores. Highly ordered and orientated hexagonal phase was observed, shown in Figure 1.10 (a), which was formed by the parallel-packed-channel (Figure 1.10 (b)).

![TEM images of the mesoporous silica rods in 400nm EPC](image1)

Figure 1.10 a, b) – TEM images of the mesoporous silica rods in 400nm EPC; b) – microtomed section of the silica rods. [43]
1.4.2 Research Objectives

In the early stage of the presented study, different results were observed from what was reported in Nature Materials by the G. D. Stucky et al. [42]. This inspired a systematical study on this project. Meanwhile based on the reported literature, few studies were investigated on organic-inorganic hybrid self-assembly in the track-etched polycarbonate (EPC) channels. Thus in this thesis project, systematical study were carried on by using well-defined pore channels of various diameters (in both AAO and EPC) as space-confinement tool, silica (TEOS) as model system, and tri-block copolymer (P123) as self-assembling template. Nano-scale effect was observed and is discussed in Chapter Three. The substrate difference between the AAO and EPC are discussed in Chapter Four. In Chapter Five, process condition effects are analyzed. As mesoporous silica nanowires could be used in producing metal or other inorganic mesoporous wires, based on the better understanding on the control of mesoporous structure of silica nanowires through this systematical study on the space-confinement polymer-TEOS self-assembly, then the fabrication of various nanowires of target meso-structure could be achieved.
Chapter Two:
Experiment
2.1 Specimen Synthesis and Processing

2.1.1 Materials

TEOS, Si(OC₂H₅)₄ purchased from J. T. Baker Inc., was the precursor of silica species. Absolute EtOH, C₂H₆O, was purchased from AAPER Alcohol Chemical Co. (absolute-200 proof). HCl aqueous solution with pH of 2.00 was prepared from diluting HCl (6.000 ± 0.030 N) provided by VWR with deionized water, and then adjusting pH via pH tester. Tri-block co-polymer P123, from BASF Corporation, was used as self-assembly template. The chemical formula of P123 is (PEO)₂₀(PPO)₇₀(PEO)₂₀ and its structure is shown in Figure 2.1.

![Figure 2.1 The schematic of the structure of P123, (PEO)₂₀(PPO)₇₀(PEO)₂₀.](image)

In this research, anodized aluminum oxide membrane (AAO) and track-etched polycarbonate membrane (EPC) were used as substrates to achieve space-confinement. The sizes of the channels used in AAO are 200, 73, 55, 35, and 13 nm; those in EPC are 200, 80, 50, 30, and 10 nm. The membrane disc size is 13 mm for both AAO and EPC. The Figure 2.2 shows...
the cross section and plain-view of AAO.

Figure 2.2 Cross section and top view of AAO with 200nm Channels: a) Cross section of the AAO membrane; b) Top view of AAO membrane. (Martin Steinhart, Presatention on Mesoscopic Structure Formation Processes within Ordered Porous Materials)

EPC is the PVP-treated standard white membranes purchased from SPI SUPPLIES. Polycarbonate is inherently hydrophobic however, in order to increase the wetability of the membrane surface; all SPI-Pore standard white membranes are given a final treatment with PVP (polyvinylpyrolodone) by SPI SUPPLIES. The polycarbonate track etch membranes by SPI do not have an inherent positive or negative charge.

The 200 nm AAO was purchased from WHATMAN. The membrane is hydrophilic and is compatible with most solvents and aqueous material. No monomers, plasticizers, adhesives, surfactants or wetting agents are used in the manufacturing process, which eliminates sample contamination and ensures low protein binding and minimal loss of sample.

The AAO with diameter less than 80 nm were collaboratively provided by Synkera. The surface of anodic alumina membranes is hydrophilic.
2.1.2 Procedure

Evaporation-induced self-assembly, sol-gel, and space-confinement are involved in the procedure. The precursor solution was prepared as follows: TEOS was pre-hydrolyzed in diluted hydrochloric acid (pH 2) and ethanol solution for 10 minutes and P123, which was initially dissolved in ethanol, was added into the TEOS solution. The mixture was stirred for three hours at room temperature. The final mass ratio of the precursor solution was 2.6 TEOS: 0.6875 P123:1.35 HCl solution (pH 2): 5 EtOH. The precursor solution was loaded into AAO or EPC channels by vacuum impregnation for one hour at room temperature, and the loaded AAO or EPC membrane was subsequently aged in ambient condition overnight. It was then calcinated to remove the polymer template and EPC substrate. The procedure is illuminated in details in Figure 2.3 by the experimental procedure flowchart. Figure 2.4 is the schematic diagram showing the concept of space-confined silica-P123 hybrid self-assembly.
Figure 2.3 The flowchart of the experiment procedure.

Figure 2.4 The schematic diagram showing the concept of space-confined silica-P123 hybrid self-assembly in channels of AAO or EPC discs.
2.2 Characterization Techniques

Determining the 3-dimensional structure of the mesoporous structure of nanowires is challenging. Usually it necessitates a combination of real space investigation with transmission electron microscopy (TEM) and reciprocal space investigation with small-angle x-ray scattering (SAXS). TEM can give the visualized morphology of the mesoporous structure, however the pore size can only be manually measured from the TEM images. SAXS can provide complemental information of the bulk average pore size. As time and funding limit, the SAXS was not used to measure the overall average pore size of the mesoporous structure in this thesis research.

STEM was primarily used to characterize the structure of the mesoscale domain. Although the STEM results might not be sufficient for the 3D structure determination, they were enough to get a view of the mesoporous structures. Meanwhile the microtome was used to characterize the cross-section of the nanowires for verifying the conjectured cross-sectional structure.

2.2.1 Preparation of STEM sample

To prepare the specimen for the STEM, the AAO or EPC substrates must be removed to get the free nanowires. EPC is removed by calcination at 550°C. Thus for the nanowires in EPC, the specimen was directly dispersed in the EtOH using ultrasonic after calcination. A drop of the suspension solution was dropped on the porous carbon coated TEM grid and dry
in air. The AAO membrane was completely dissolved in 5 M HCl at 60°C for approximately one hour.

The cross-section specimen of silica wires were prepared by microtome. The epoxy used to make the microtome block is Araldite 6005 and it was cured overnight in an oven at 60°C. The ultramicrotome used is a Leica Ultracut UCT with a Diatome diamond knife at a 4°clearance angle. The microtome samples were prepared by Kimberly Shawn Reeves, ORNL.

2.2.2 STEM

STEM, scanning transmission electron microscope is a type of transmission electron microscope. The mechanism of STEM is shown in Figure 2.5. The STEM was developed at about the same time as the TEM; however, its development was much slower than that of the TEM until the work of A.V. Crewe [44] demonstrated the potential of STEM. STEM offers many things over using TEM and SEM separately, such as 1) enhanced contrast because chromatic aberration is removed, the elimination of unwanted diffraction contrast in strained materials; 2) much improved penetration (about 10x compared to TEM); 3) unique imaging modes including the quantitative Z-contrast mode; 4) SE, BSE, and low loss imaging modes for thicker and bulk samples; 5) a painless upgrade path for SEM operators.

In this thesis project’s characterization Hitachi HD-2000 STEM was used and was performed
at beam energy of 200 keV. There are three modes that can be used to take images: SE, Z-contrast (ZC) and TE mode. For the SE and ZC mode, the white areas represent silica and it contrary in the TE mode.

For each sample of silica wires, at least three different observed spots were randomly chosen and usually eight to ten images of different position of silica wires were taken to present the overall reliable morphology of mesoporous structure. The percentages of a certain mesostructure and pore sizes of the mesostructures were estimated from the STEM images.

Figure 2.5 Schematic of Scanning Transmission Electron Microscope. (Powerpoint of Introduction to STEM by Dr. Vinayak P. Dravid, Northwestern University)
Chapter Three:
Nano-Scale Channel Size Effect of AAO and EPC on Mesoporous Structure of Silica Wires
3.1 Nano-Scale Channel Size Effect of AAO Channels

As discussed in Chapter One, the AAO channels are around 200 nm in diameter with two major mesoporous structures of silica wires have been reported: 1) the long axes of the mesopores aligned with the long axes of the AAO channels (columnar orientation); 2) the mesopore aligned in the axial direction (circular orientation). G. D. Stucky et al. [42] carried out a systematical study in AAO channels that were less than 80 nm in diameter. They reported silica mesostructures with chiral mesopores such as single and double-helical geometries. In this thesis study contrary structures are reported: a uniformed air-sphere-array structure in the mesoporous silica wires formed in AAO channels less than 80 nm as well as mixed mesoporous structures of the silica wires formed in 200 nm AAO channels. Previously reported structures were only a portion of the observed mixed mesoporous structures.

3.1.1 The Silica Wires in 200 nm AAO Channels

The mesoporous structures of the silica wires formed in the 200 nm AAO are mixed mesoporous structure: worm-like structure (the upper wire of Figure 3.1(a)); cubic structure and lamellar structure as shown in Figure 3.1(b); ordered and orientated hexagonal structure with lamellar in the center as shown in Figure 3.1(c). The hexagonal structure in Figure 3.1(c) has pore diameter $10 \pm 1$ nm, which is larger than the typical pore size of MCM-41, 7.5 nm.
A cross-sectional view is needed to verify the 3-D structure of the highly ordered structure shown in Figure 3.1 (c). From the side-view, three possible cross-sectional-view structures were proposed which are shown in Figure 3.2: circular-channel (model-a); radial-channel (model-b); parallel-packed-channel (model-c).

![Figure 3.1](image)

Figure 3.1 Representative STEM images (ZC MODE) of silica wires formed in 200 nm AAO. (a) Ordered hexagonal pores along the edge of the wires but worm-like disordered structure in the center of the wires; (b) ordered hexagonal pores along the edge of the wires and mix domain of worm-like structure, lamellar phase and cubic structure in the center; (c) Ordered and orientated hexagonal structure with rod-packed structure in the center.
Figure 3.2 Schematic representation of three possibilities for 200 nm silica wires with ordered and orientated hexagonal side-view: (a) circular-channel as model-a); (b) radial-channel as model-b; (c) parallel-packed-channel as model-c. *The scale in the schematic does not represent the real scale.*

To verify which model of the three possible cross-section structure best describes the highly ordered and orientated hexagonal structure with lamellar in the center in 200 nm silica wire, microtome and STEM were used to characterize the cross-section of the silica wires. The cross-sectional images revealed that the structure of the model-a was observed as shown in Figure 3.3 (a, b) and that circular structure occupied around twenty-five percent of the whole mesoporous structures of silica wires. The structure similar to the model-b was not observed. The structure similar to model-c was observed (Figure 3.3 (c)) however this parallel-packed-channel structure was rare observed (less than one percent). Contrarily, the circular-channel structure is relatively easy to observe as shown in Figure 3.4, although it’s usually the mixture of circular-channel and columnar-channel. Meanwhile the ZC image of Figure 3.3 (b) (part of the cross-sectional-view and part of the side-view of the silica wires) illuminated that when the cross-section-view is circular structure (model-a), the side-view is exactly the same as the ordered and orientated hexagonal structure with packed-channel structure in the center. Thus model-a has the most possibility to be the cross-sectional view
of the ordered and orientated hexagonal structure with packed-channel structure in the center.

Figure 3.3 Representative STEM images of cross-sectional-view of silica wires: (a) circular structure, TE mold; (b) cross-section and side-view of circular structure, ZC mold; (c) parallel-rod structure ZC mold; (d) columnar structure, ZC mold.
Figure 3.4 Representative STEM images of cross-section-view of silica wires (ZC MOLD).
The three-shell circular-channels structure was schematically shown in Figure 3.5 for better understanding of the structure. This observation complied with what literature reported as the mesopores aligned in the axial direction or circular orientation. The structure shown in Figure 3.3 (d) was reported in literature and observed in this study, although it does not exist as frequently as circular-channel structure. Figure 3.3 (d) shows the long axes of the mesopores aligned with the long axes of the AAO channels, columnar orientation.

Figure 3.5 3-D schematic of circular-channels structure: a) side view; b) side view without some circular channels for better illumination of the structure; c) bottom-side view; d) top-view.
As discussed above, the literature reported mesoporous structure in the silica wires were observed however the circular structures only occupied twenty-five percent of all mesoporous structures. The mesoporous structure of ordered hexagonal pores along the edge of the wires but worm-like disordered structure in the center is the dominant structure (more than fifty percent). The ordered structure prefers formation in the vicinity of the AAO channel walls (edge-more-ordered phenomenon) and the structural order becomes slightly disordered in the interior region. This phenomenon was also observed on the synthesis of thin film of mesoporous silica [45]. It was reported that the highly ordered mesoporous structures of silica were observed in the vicinity of the substrate surface and the structural orders tended to be disordered in the region far from the substrate surface. A. Yamaguchi et al. [46] also reported the similar edge-more-ordered phenomenon in mesoporous structure of the silica wires formed in 200 nm AAO channels; they used CTAB as the self-assembly template and explained that the AAO channel wall could absorb CTAB and the CTAB micelles could be formed at the channels wall even if the CTAB concentration in the interior is below the critical micelle concentration. In the situation of P123 as self-assembly template here, because the AAO substrate (ceramic) is friendlier to silica species (ceramic) than to P123 (polymer) and the silica species interact with P123 micelles by hydrogen-bond, when the AAO wall attracts the silica species, it also increases the concentration of the P123 in the vicinity of the AAO wall, even if the concentration of the P123 in the solution is below the critical micelle concentration (CMC). Thus the order of the mesostructure spread from the silicawires surface to interior.
3.1.2 The Silica Wires in AAO Channels Less than 80 nm

3.1.2.1 Side-View of Silica Wires in AAO Channels Less than 80 nm

Neither columnar nor circular-channel structures were observed in the silica wires formed in AAO channels with diameter less than 80 nm. The phenomenon of structural order from the vicinity of AAO wall was also not observed. As shown in STEM images (Figure 3.6), a uniformed air-spherical-array structure was primarily observed in the mesoporous silica wires formed in AAO channels with diameter less than 200 nm. This is different to the reported results in the Nature Materials by G.D. Stucky’s et al. [42], in which the chiral mesoporous structures were the dominate structure. In the current results the spiral structures were observed but exists in minimal amounts (less than five percent), Figure 3.6 (b, d). Thus, there could be more than one mesoporous structure of the silica wires formed in AAO channels with diameter less than 80nm.

As clearly observed in Figure 3.6, there is one row of air-sphere in the wires of 15 ± 5 nm diameter; two rows in the wires of 32 ± 5 nm diameter; it rises to three and four rows when the diameter of the wires is 43 nm and 50 nm, respectively. Note the air-sphere rows alignment complies with the shape or diameter variation of the AAO channels (Figure3.6 (a)), indicating the efficient AAO channel confinement effect. The diameter of the air-sphere is 13.5 ± 1 nm, which indicates how the diameter of the AAO channels confines the number of the hollow-sphere rows: N ≈ D/13.5; N is the number of the hollow sphere rows; D is the
diameter of AAO channels.

Figure 3.6 Representative STEM images (ZC MOLD) of silica wires formed in AAO channels: a, b) 13 nm; c, d) 35 nm; e) 55 nm; f) 73 nm. The spiral structures are presented in b) and d).
3.1.2.2 The 3-D Structure of Silica Wires in AAO Channels Less than 80 nm

From the Figure 3.6 (e), it seems that the mesoporous structure of silica wires with diameter less than 200 nm is geometrically constructed by coiling 2-D hexagonal thin films. Thus the cross-sectional view of the wires was characterized to verify the 3-D structure of the silica wires with diameter less than 200 nm. The cross-sectional view of silica wires formed in both 73 nm and 35 nm AAO channels reveal that the silica wires with diameter less than 200 nm have 3-D structure that consists of air-sphere arrays (Figure 3.7 & 3.8). The P123 sphere micelles seem to form by hexagonal-close-packing, if geometrically allowed, in the AAO channels and the silica species occupied the rest of the area; after calcinations, the P123 were removed and left as the air-sphere.

Figure 3.7 Representative STEM images (ZC MOLD) of silica wires formed in 73 nm AAO channels. Inside the circle is the the cross-section of the wires and rest of that wire is the side-view, which reveals that they are porous wires not porous-wall tubes.
In summary, the confined mesostructures prefer to curve themselves within the AAO channels in order to comply with the geometry constraint. The air-sphere-array structure in the silica wires is only formed in the AAO channels with diameter less than 80 nm. The number of the air-sphere rows can be predicted by the relationship between the diameter of AAO channels and the diameter of the air-sphere.
3.2 Nanoscale Channel Size Effect of EPC

Compared to the studies on silica wires in AAO channels, studies of silica wires in EPC channels are really countable. As best as can be known, only Z. Liang and A.S. Susha [43] reported the P123-silica hybrid self-assembly in EPC channels. Their work was focused on the silica wires in 400 nm EPC channels where parallel-packed-channel with ordered hexagonal side-view was dominantly observed, shown in Fig 1.10. Contrary to these reported results, the samples from the 400 nm silica wires of the current study’s had mixed mesoporous structures. The systematical study of the silica wires formed in the EPC channels with diameters less than 400 nm is presented in the following discussion.

3.2.1 The Silica Wires Formed in 400 nm EPC Channels

The silica wires in 400 nm EPC had mixed phase (side-view) such as 2-D hexagonal (Figure 3.9 (a)), ordered lamellar perpendicular to the wire axis (Figure 3.9 (b)), mixed lamellar domains with different orientation (Figure 3.9 (c)), and packed-channel structure (Figure 3.10). The transformation from hexagonal to lamellar was also observed (inside the circle of Figure 3.9 (c)). The 2-D hexagonal structure in Figure 3.9 (a) has pore diameter $8.0 \pm 0.5$ nm and pore-to-pore distance $11 \pm 1$ nm. The lamellar structures in both Figure 3.9 (b) and (c) have layer-to-layer distance of $11 \pm 1$ nm. The space-distance of both hexagonal and lamellar is $11 \pm 1$ nm indicating that during the transformation from hexagonal to lamellar the space distance remains unchanged.
Figure 3.9 Representative STEM images (ZC MODE) of the silica wires formed in 400nm EPC: a) highly ordered 2-D hexagonal structure (average pore diameter of 8 nm; average space distance of 11 nm); b) ordered lamellar structure perpendicular to the wire axis (average space distance of 11 nm); c) lamellar domains with different orientation and inside the circle indicate the transformation from hexagonal to lamellar.
A packed-channel structure is revealed in Figure 3.10, although that structure turned into a worm-like structure when approaching the other side of the wire edge. From the right edge of the wire, the channel mouth could be observed and the morphology of channel mouth arrays is 2-D hexagonal.

Figure 3.10 Representative STEM images (ZC MODE) of the silica wires formed in 400 nm EPC: a,b) packed-channel structure.

### 3.2.2 The Silica Wires Formed in 200 nm EPC Channels

The mesoporous structure of 200 nm silica wires formed in EPC channels also has mixed mesoporous structures (Figure 3.11). The worm-like structure is the primary structure observed (more than fifty percent). Figure 3.11 (c) suggests that during the transformation from hexagonal to lamellar, there are two steps: 1) the worm-like structure first turns to channels; 2) the channels turns to lamellar. In the first step, the orientation of channels is randomly formed, which makes the different orientation of lamellar (step two).
Figure 3.11 Representative STEM images (ZC MODE) of side-view of mesoporous silica wires formed in 200 nm EPC: (a) worm-like structure; (b) mixed domain of worm-like structure, lamellar, and transition from hexagonal to lamellar; (c) the cross-sectional view of the transition from hexagonal to lamellar side-view.
3.2.3 The Silica Wires Formed in EPC Channels No Larger than 80 nm

The mesoporous structure of 80 nm silica wires formed in EPC channels has mixed architecture (Figure 3.12). The worm-like structure is the primarily observed structure (more than fifty percent).

Figure 3.12 Representative STEM images (ZC MODE) of side-view of mesoporous silica wires formed in 80 nm EPC: (a) worm-like structure; (b) mixed domain of lamellar, transition from hexagonal to lamellar and amorphous structure; (c) mixed domain of hexagonal, transition from hexagonal to lamellar and amorphous structure.
For silica wires formed in 50 nm EPC channels, the worm-like structure (Figure 3.13 (a, b)) is the primarily observed structure (more than ninety percent) and only a few structure transformation from hexagonal to lamellar existed. The pore diameter of the worm-like pore-structure is $8.0 \pm 0.5$ nm. Figure 3.13 (g) illuminates the surface morphology of the 50 nm silica wires; the wire surface has continuous bump structure.

A more ordered worm-like structure (Figure 3.13 (c, d)) was observed in the silica wires formed in 30 nm EPC. That structure have the hint of hexagonal pattern however not as ordered as the 2-D hexagonal phase (Figure 3.9 (a)). The pore diameter of the hexagonal is $8.0 \pm 0.5$ nm. This structure will be referred to as a random hexagonal structure. Random hexagonal is the primary structure (more than ninety percent) observed in silica wires formed in 30 nm EPC and a few structure transformations from hexagonal to lamellar existed.

The mesoporous structure in the silica wires formed in 10 nm EPC channels seems to be like the packed-air-sphere (Figure 3.13 (e, f)) and this packed-air-sphere structure is the dominate structure (more than ninety nine percent) in the wires formed in 10 nm EPC. The air-sphere has diameter $8.0 \pm 0.5$ nm. The wires with smaller diameter are easier damaged by the STEM beam and under the beam the wires were soon contaminated by the beam.
Figure 3.13 Representative STEM images (a-f are ZC MODE and g is SE MODE) of side-view of mesoporous silica wires formed in EPC with: (a, b, g) 50 nm channels; (c, d) 30 nm channels; (e, f) 10 nm channels.
### 3.3 Discussion of Nano-Scale Effect

In silica wires formed in both AAO and EPC channels, the silica wires with larger diameter (80 nm, 200 nm, and 400 nm) tended to form mixed domains and the single domain favorably formed in silica wires with smaller diameters (10 nm, 30 nm and 50 nm). According to C. J. Brinker [16], at a given vapor pressure, larger pores dry faster because all menisci have the same curvature. Thus larger channel diameter means faster solvent evaporation and less time for the equilibrium of silica-P123 hybrid self-assembly structure. Smaller channels give longer time for the equilibrium and lead to more uniformed mesoporous structures.

Meanwhile, the longer time for the evaporation also means the longer time for the silica species to form larger pieces via the sol-gel, which can fix the mesostructure of the P123 micelles in the sphere. The smaller size of space-confining substrate channels could also have the spatial hindrance for the P123-silica hybrid self-assembly to lamellar structure. Moreover, according to J. Israelachvili [47] even in the absence of any attractive wall-micelle interaction, geometric considerations of the channels alone dictate that the micelle must reorder themselves so as to be accommodated among the wall. Thus smaller channel size dictates larger geometric confinement, and produces more uniform and ordered mesoporous structure.
Chapter Four:
Substrate Effect between AAO and EPC on Morphology of Mesoporous Structure of Silica Wires
4.1 The Mesostructure Morphology Differences of Silica Wires formed in between AAO and EPC

Through results and discussion of Chapter Three, there are several substrate effects observed between AAO and EPC channels, which are summarized below:

1) The edge of the silica wires formed in AAO is smoother than that in EPC as shown in Figure 4.1. This phenomenon was observed in all the silica wires with diameter less than 200 nm. A clear line can be observed along the edge of wire formed in AAO channels in the STEM images, which seems as the AAO wall attracted the silica species and a silica shell formed along the AAO channel wall. The silica wires formed in EPC channels have pits along the wire edge which are especially significant for the 10 nm silica wires (Figure 4.1(a)).
It’s conjectured that the AAO substrate (ceramic) is friendlier to silica species (ceramic) than to P123 (polymer), so silica species accumulate in the vicinity of AAO channel wall and separate the AAO wall from P123 micelles. Thus the silica species aggregating and networking along the AAO walls form a smooth silicawire surface. Contrarily, the EPC substrate does not have the friendly contact with silica species and instead prefers contact with P123 micelle so that no smooth surface is formed for the silica wires in EPC channels. This conjecture is schematically shown in Figure 4.2.
2) The edge-more-ordered phenomenon (as discussed in 3.1.1 that the ordered structure prefers formation in the vicinity of the AAO channel wall, and the structural order becomes slightly disordered in the interior region) was only observed in 200 nm AAO, not in the 200 nm EPC. One explanation is that AAO channels assist the self-assembly of silica-P123 hybrid. The possible mechanism may be explained by the interaction between the AAO wall and the self-assembly silica-P123 hybrid. Because the silica species interact with P123 micelles by hydrogen-bonding, when the AAO wall attracts the silica species it also increases the concentration of the P123 in the vicinity of the AAO wall, even if the concentration of the P123 in the solution is below the critical micelle concentration (CMC). Moreover,
according to J. Israelachvili [46] even in the absence of any attractive wall-micelle interaction, geometric considerations of the channels alone dictate that the micelle must reorder themselves so as to be accommodated among the wall. Thus the order of the mesostructure spread from the silica wires surface to interior.

3) The circular-channel structure (Figure 3.2 (a)), which occupied twenty-five percent of the mesostructure of silica wires formed in 200 nm AAO, was not observed in silica wires formed in 200 nm EPC. There is one suggestion that “the curvature of the AAO channel wall may drive the micelles towards the circular orientation” [40]. However if the “curvature” is the driving force, the same circular-channels structure should also be formed in EPC channels. Thus it is not so simple to say that just the curvature of the channel wall is the driving force, but also may be the substrate surface wetability, Hamker constant and physical properties (hard or soft materials) etc. Meanwhile the slightly observed (less than five percent) chiral mesoporous structures of silica wires formed in AAO (Figure 3.5) was not observed in silica wires formed in EPC for any of the nano-scales. It’s conjectured that the driving force for the silica wires formed in AAO is somewhat different from that in EPC and these differences cause the circular-channel structure and chiral mesoporous structures to only be produced in AAO channels. However what are the differences of driving-force and how the differences lead to the formation of circular-channel and chiral mesoporous structures are still under research.

4) Another mesostructure morphology difference is that the mesopore size in silica wires formed in AAO channels (13.5 ± 1.0 nm) is larger than those (8.0 ± 0.5 nm) in formed in
EPC when silica wires have diameter less than 200 nm, as shown in Figure 4.3. As the micelle of the P123 in the solution is shown in Figure 4.4, larger air-sphere structure in the silica wires indicates the more expanded PEO and, especially, PPO chains. A lot of factors may affect the size of micelle, such as the block chain length, solution composition, and temperature etc. For the PEO-PPO system, longer PEO chain leads to smaller pore-size of mesoporous materials [48]. The lattice spacing increases as the weight percentage of P123 decreases [49]. As will be discussed in Chapter Five (Chapter 5.3), higher air-dry temperature leads to smaller pore size. However in the situation of this thesis project, the synthesis and processing conditions are the same for silica wires formed in AAO and EPC channels with size from 10 nm to 200 nm scales (the samples presented in Chapter Three). A possible explanation is that the AAO substrate attracts more silica species into the substrate channels and leads the weight percentage of P123 in AAO channels to be lower than that in EPC channels, which indicates the larger pore size. It needs to be pointed out that the calcination temperature and time for silica wires formed AAO (600°C, 0.5hr) and EPC (550°C, 5hr) are different. The calcination condition differences might be the factor that causes the pore size difference. However as to be discussed in Chapter Five, higher temperature leads to smaller pore size, had this been caused by the calcination temperature the pore size of silica wires formed in AAO would have been smaller than that in EPC.
Figure 4.3 Representative STEM image (ZC MOLD) of silica wires: a) silica wires formed in 55 nm AAO channels; b) silica wires formed 50 nm EPC channels.

Figure 4.4 Schematic of P123 micelle: inside green chain represents PPO block and outside red chains represent PEO block. The silica species react with PEO chain via hydrogen-bonding.
4.2 The Morphology Differences of AAO and EPC Channels

As shown in Figure 4.6, the pore-density of AAO substrate is higher than that of EPC. Thus when the AAO and EPC substrates are both 13 mm diameter discs, the AAO substrate could produce more silica wires. Meanwhile the thickness of AAO is 60 µm which is thicker than that of EPC (6 to 14 µm), which means AAO substrate could also produce longer wires. EPC substrate as polymer can be removed with P123 template by one step, while AAO has to be removed by additional acid-dissolution. In another hand AAO substrate can also remain to hold the wires when P123 template is removed, which is convenient for using the silica wire as a template to produce other inorganic wires.

![Representative SEM images of the surface of AAO and EPC substrate: a) AAO; b) EPC.](image-url)

Figure 4.6 Representative SEM images of the surface of AAO and EPC substrate: a) AAO; b) EPC.
Chapter Five:
Effects of Processing Conditions on Morphology of Mesoporous Structure of Silica Wires
5.1 Effect of Precursor Solution Aging Time

As shown in the procedure flowchart in Chapter two, the aging time means the time span of stirring the mixed solution of surfactant and precursor solutions. Thus the aging time directly affect the size of the silica species in the solution which was later filled into the substrate channels. Longer aging time produced larger silica species and the larger silica species means more spatial hindrance to the self-assembly of the P123-silica hybrid, meanwhile the steric hindrance-effect is more significant in the smaller scale substrate channels. Figure 5.1 is the STEM images of the silica wires formed in 50 nm EPC channels with aging times of 0.03, 1.5, 3, and 48 hours. From random but abundant observations, it was seen that the worm-like structure is the major structure in all of the aging time samples; yet, more lamellar structure was observed when aging time was 0.03 hours and the completely amorphous structure was only observed when aging time was 48 hours.
Figure 5.1 Representative STEM images (ZC MOLD) of the silica wires formed in 50 nm EPC when aging time was 0.03, 1.5, 3, and 48 hours.

The same experiment was also carried out in the 200 nm EPC channels for different aging times (Figure 5.2). The same trends were observed, however the most lamellar structure was observed when aging time was 1.5 hours. This means that only when the silica species is very small (aging time only 0.03 hours) does the size of silica species not hinder the self-assembly into lamellar phase for the 50 nm EPC channels, meanwhile the critical time for self-assembly in 200 nm EPC is 1.5 hours. As the normal experiment conditions is aging time of 3 hours, the common observed structure is the worm-like structure in the nano-scale-effect (Chapter 3.2.2 & 3.2.3) samples.
Figure 5.2 Representative STEM images (ZC MOLD) of the silica wires formed in 200 nm EPC when aging time was 0.03, 1.5, 3, and 48 hours.
5.2 VER Effect

There were two vacuum-evaporation-rates (VER) achieved in the experiments by two kinds of solution containers: vials and petri dishes. The mouth size differences of the two containers changes the rate of the solvent evaporation under the same vacuum. The relative value of the VER was measured and it was found that the average high VER is 1.46 times the average low VER.

The silica wires formed in 200 nm AAO channels under two VER were compared. In both cases the silica wires have mixed mesoporous structure and circular-channel structure were observed in both samples. Circular-channel structure of silica wires under higher VER have channel-pore-size of 10.0 ± 0.5 nm, which is the same as that under lower VER. Thus the VER during the vacuum impregnation does not affect the channel-pore-size of the circular-channel structure.

A packed-disc structure (less than twenty percent) was observed in the silica wires formed in 100 nm EPC under high VER. The discs are perpendicular to the wire axis as shown in Figure 5.3. The layer-to-layer distance is 11 ± 1 nm. No similar structure was observed in the silica wires formed in 100 nm EPC under low VER and no similar structure is reported. From random but abundant observations, it could be concluded that lamellar structure is preferred under high VER for the silica wires formed in 100 nm EPC, although the orientation of the lamellar structure may be perpendicular to the axis, or along the axis, or
have an angle to the axis. It’s conjectured that the higher VER only produced suitable timing for the silica species to grow big enough to fix the lamellar structure; under lower VER when the P123/water ratio for lamellar phase was achieved, the silica species already big enough to hinder the phase transformation.

Figure 5.3 Representative STEM image (ZC MOLD) of silica wire formed in 100 nm EPC under lower VER with the lamellar disc perpendicular to the wire axis.

Figure 5.3 Representative STEM image (ZC MOLD) of silica wire formed in 100 nm EPC under lower VER with the lamellar disc perpendicular to the wire axis.
5.3 Air-Dry Effect

As shown in the procedure flowchart in Chapter Two, air drying is the process just after vacuum impregnation. The solution-soaked substrate discs were dried in air. The effects of different air drying conditions on the mesoporous structure of silica wires were investigated.

With 60ºC air blow dry (which was achieved by hair-dryer) condition, a unique structure was observed in the silica wires formed in 200nm AAO as shown in Figure 5.4 (a). The mesoporous structure in Figure 5.4 looks like the packed-lamellar aligned along the wire axis. However as this lamellar along the axis structure hardly exist (less than one percent), it’s almost impossible to relocate and verify the 3-D structure by other measurements. The parallel-packed-channel structure with the channels perpendicular to the wire axis, which was only reported by Z. Liang and A.S. Susha [43] in silica wires formed in 400 nm EPC was also slightly (less than five percent) observed in the silica wires formed in 200 nm AAO at 60ºC air blow dry as shown in Figure 5.4 (b). The pore size is 5.5 ± 0.5nm, which is smaller than that observed in silica wires formed in 400 nm EPC, 8.0 ± 0.5 nm (Figure 3.9 (a)) and smaller than all the pore size observed in silica wires formed in AAO under normal synthesis and processing conditions (Chapter 3.1). The pore size of the circular-channel structure of silica wires formed in 200 nm AAO at 60ºC air blow dry is also 5.5 ± 0.5 nm (Figure 5.4 (c)), is also smaller than that by ambient air dry, which is 10.0 ± 0.5 nm (Figure 3.1 (c)).

Thus it seems the elevated temperature air blow dry leads to smaller pore size. The
following-up experiment demonstrated that it was the temperature plays the role on the air-dry effect not the air blow.

Figure 5.4 Representative STEM images (ZC MOLD) of silica wires formed in 200 nm AAO by 60°C air blow dry: a) parallel lamellar along the axis; b) parallel-packed channels; c) circular-channels.
Regarding the lamellar structure of silica wires formed in 200 nm EPC there is no significant space distance difference made by between ambient air dry and 60ºC air blow dry. The only difference is that under 60ºC air blow dry condition the mesoporous structure of silica wires prefer lamellar and amorphous structures (Figure 5.5) over the worm-like structure (Figure 3.11 (a, c)).

Figure 5.5 Representative STEM image (ZC MOLD) of silica wires formed in 200 nm EPC at 60ºC air blow dry.
Chapter Six:
Conclusion and Suggestion for Future Work
6.1 Conclusion

In the study of mesoporous silica wires by space-confined silica-P123 hybrid self-assembly, nanoscales effect, substrates effect and the processing conditions effects on the mesoporous structure were investigated.

1) In silica wires formed in both AAO and EPC channels, the silica wires with larger diameter (80, 200, and 400 nm) tend to form mixed mesoporous structures and the single domain favorably formed in silica wires with smaller diameters (10, 30, and 50 nm). The smaller channel size leads larger geometric confinement, and produces more uniform and ordered mesoporous structure. The mesostructure of silica wires formed in 200 nm AAO channels have mixed structures of circular-channel, columnar-channel, worm-like structure, and more. A uniform air-sphere-array structure with sphere diameter $13.5 \pm 1.0$ nm in the mesoporous silica wires formed in AAO channels that are less than 80nm, is different from the results reported by G.D. Stucky et al. [42]. The mesoporous structure of silica wires formed in 400 nm EPC channels had mixed phase, including the parallel-packed-channel structure which was reported by Z. Liang and A.S. Susha [43] and the lamellar structures with different orientation, etc. As listed in Table 6.1 the ratio of TEOS: P123: HCl (pH 2):EtOH used in this thesis project and were almost the same as that used by G.D. Stucky et al meanwhile the concentration of HCl used by Z. Liang and A.S. Susha is slightly higher. The mesostructure in silica wires formed in 80 nm and 200 nm EPC channels were mixed phase with the worm-like structure being the most common structure observed. For the silica
wires formed in 30 nm and 50 nm EPC channels, the worm-like structure was the primarily observed structure (more than ninety percent); for those in 10 nm EPC channels the packed-air-sphere was the dominating structure. The pore-sizes observed in the silica wires formed in EPC were all around 8 ± 0.5 nm.

Table 6.1 The mixture ratios used in this thesis project and by G.D. Stucky et al [42] and Z. Liang and A.S. Susha [43]

<table>
<thead>
<tr>
<th></th>
<th>Ratio</th>
<th>TEOS</th>
<th>P123</th>
<th>H₂O</th>
<th>HCl</th>
<th>EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thesis project</td>
<td>Mass</td>
<td>2.6</td>
<td>0.6875</td>
<td>1.35,HCl solution pH=2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Molar</td>
<td>1</td>
<td>0.0096</td>
<td>6</td>
<td>0.0010</td>
<td>8.7</td>
</tr>
<tr>
<td>G.D. Stucky</td>
<td>Mass</td>
<td>2.08</td>
<td>0.552</td>
<td>1.080364,HCl solution pH=2</td>
<td>4.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Molar</td>
<td>1</td>
<td>0.0096</td>
<td>6</td>
<td>0.0010</td>
<td>8.8</td>
</tr>
<tr>
<td>Z. Liang and A.S. Susha</td>
<td>Mass</td>
<td>2.08</td>
<td>0.5462</td>
<td>1.08</td>
<td>0.0032</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>Molar</td>
<td>1</td>
<td>0.0095</td>
<td>6</td>
<td>0.0089</td>
<td>8.7 (for tube)</td>
</tr>
</tbody>
</table>

2) Differences in the morphology of silica wires were observed between the silica wires formed in AAO and EPC. The edge of the silica wires formed in AAO is more smooth and sharp than that in EPC. The edge-more-ordered phenomenon (the ordered structure prefers formation in the vicinity of AAO channel walls, and the structural order becomes slightly disordered in the interior region) was only observed in 200 nm AAO, but not in the 200 nm EPC. The circular-channel structure (Figure 3.2 (a)), which occupied twenty-five percent of the mesostructure of silica wires formed in 200 nm AAO, was not observed in silica wires
formed in 200 nm EPC. Another mesostructure morphology difference is that the meso-pore size in silica wires formed in AAO channels (13.5 ± 1.0 nm) is larger than those formed in EPC (8.0 ± 0.5 nm) in silica wires with diameter less than 80 nm. EPC substrate as polymer can be removed with P123 template by one step, while AAO has to be removed by acid-dissolution. Conversely, the AAO substrate can remain to hold the wires when P123 template is removed, which is convenient for the application of silica wires as template to produce other inorganic wires.

3) For the silica wires formed in 50 nm and 200 nm EPC channels, lamellar structure was preferred by less aging time and 48 hours aging time leded to an unstructured phase. A packed-disc structure where the discs are perpendicular to the wire axis was observed in the silica wires formed in 100 nm EPC under high VER. The diameter of the channels of the circular-channel structure in silica wires formed in 200 nm AAO decreased as the air-dry temperature increased.

4) It’s concluded that the obtained self-assembly structure is very sensitive to the experimental parameters, such as the concentration of both silica precursor and polymer template, temperature, reaction time, space-confining substrate properties, etc. The obtained mesoporous structure depends not only the thermodynamics of the equilibrium of the P123 self-assembly but also on the size of the silica species. When the size of silica species is large enough, the silica species could pose a steric hindrance effect on transformation and equilibrium of self-assembly structure and this steric hindrance effect becomes more
significant when the substrate channel diameter become smaller. Thus the block polymer and the inorganic precursor undergo a cooperative self-assembly, which means the self-assembly of the triblock copolymer is interfered and even hindered by the sol-gel of inorganic precursor, and the final self-assembly structure is the result of timing trade-off between equilibrium of P123 self-assembly and sol-gel of the silica precursor.
6.2 Suggestion for Future work

Although more understanding on the space-confined P123-silica hybrid self-assembly are obtained through these positive results, there are still existing questions waiting for answers. For example: what is the driving force of the circular-channel structure? Why was the circular-channel structure only observed in the silica wires formed in AAO and not in EPC when the compositions and experimental conditions were the same? As the orientation of the cylinder was randomly arranged while the transformation from worm-like structure to cylinder-arrays is there any external force or field could be applied to control the orientation? What processing parameter(s) play the role to make the difference mesoporous structure in the silica wires produced by between G.D. Stucky et al. [42] and author, when the solution composition was the same?

To answer those questions or to further understand these issues, the P123 self-assembly in the substrate channels should be conducted to simplify the system for better understanding. In-situ monitoring the transition of P123 self-assembly in substrate channels could be conduct by small angle X-ray scattering. The substrate effect could be further investigated by using the functionalized AAO channel wall (hydrophilic or hydrophobic) to understand the driving force for the circular-channel structure. The time dependence of size of silica species could be conducted by Dynamic Light Scattering. A better set-up to control the VER should be established and then the optimal VER could be found to well control the morphology of the mesostructure of silica wires. The controllable mesoporous structure of the nano-scale silica
wires will promote the synthesis of other mesoporous inorganic wires and the application of them.
References


[38] G. Kickelbick, Formation of Hexagonal Mesoporous Silica in Submicrometer Channels,
Mesoporous Silica Nano Wires by Space-Confined Self-Assembly  

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Small 1, 168 (2005)