

US-Japan Winter School on New Functionality in Glass
Kyoto University, Kyoto, Japan, January 15, 2008

Role of alkoxysilanes for the design of silica-based nanomaterials

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Technology, Waseda University
CREST, Japan Science and Technology Agency**

OUTLINE

Background

Mesoporous materials

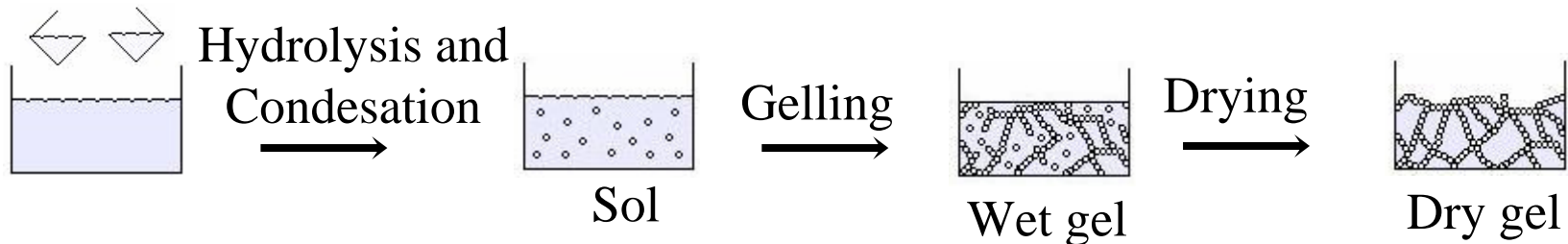
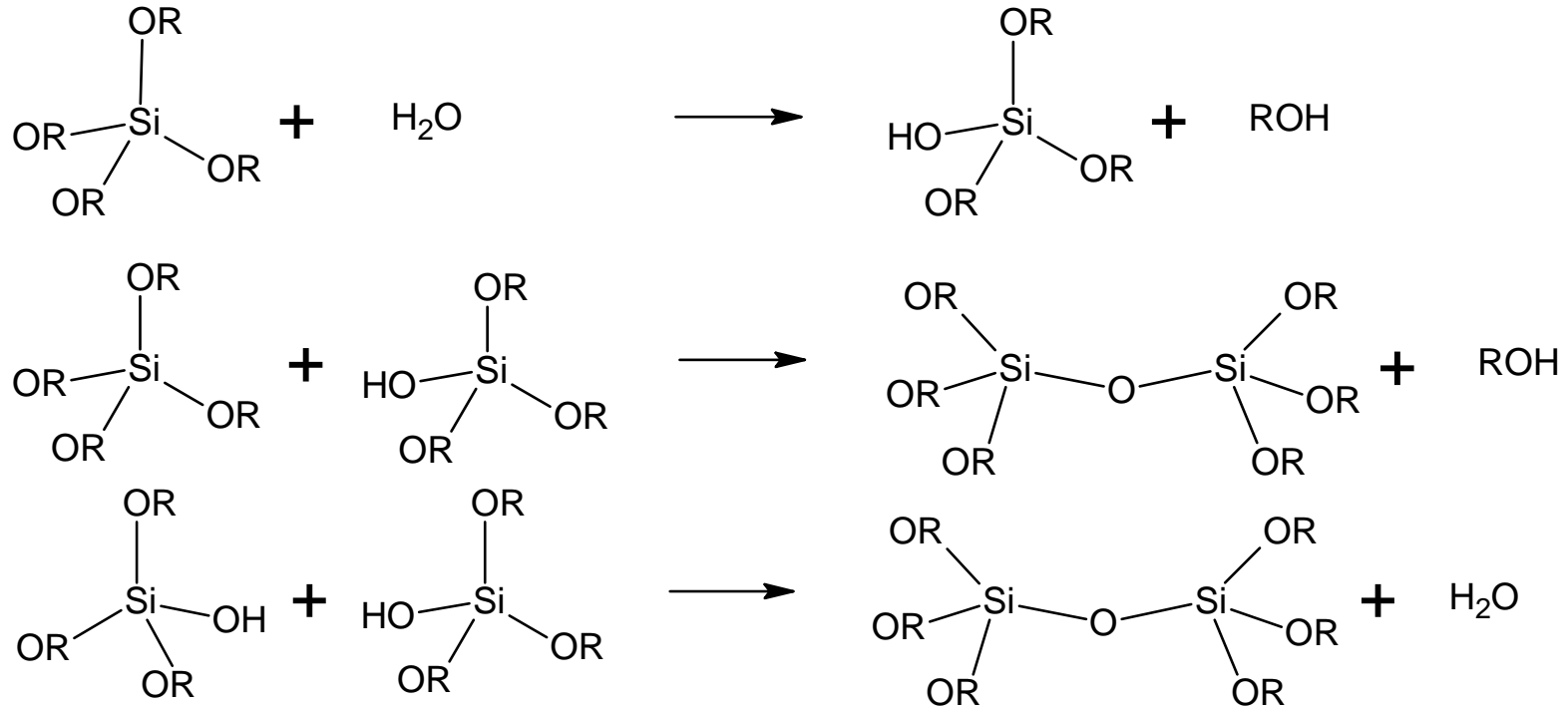
Mesoporous films utilizing alkoxysilanes

Design of alkoxysilanes and self-assembly

Varieties and possibilities

SOL-GEL Process

A. K. Varshneya, Fundamentals of Inorganic Glasses, p. 521-530.



Morphological control: Fiber, Thin film, Bulk glass, etc.

Some Advantages of the Sol-Gel Method over Conventional Melting for Glass

Brinker & Scherrer, "Sol-Gel Science", (1990) Ch. 14 Table 1

1. Better homogeneity from raw materials.
2. Better purity from raw materials.
3. Lower temperature of preparation.
 - a. Save energy;
 - b. Minimize evaporation loss
 - c. Minimize air pollution;
 - d. No reaction with containers;
 - e. Bypass phase separation;
 - f. Bypass crystallization;
4. New noncrystalline solids outside the range of normal glass formation.
5. New crystalline phases from new noncrystalline solids.
6. Better glass products from special properties of gel.
7. Special products such as films.

Some Disadvantages of the Sol-Gel Method

Brinker & Scherrer, “Sol-Gel Science”, (1990) Ch. 14 Table 2

1. High cost of raw materials.
2. Large shrinkage during processing.
3. Residual fine pores.
4. Residual hydroxyl.
5. Residual carbon.
6. Health hazards of organic solutions.
7. Long processing times.

Tetraalkoxysilanes

Tetraalkoxysilanes $\text{Si}(\text{OR})_4$

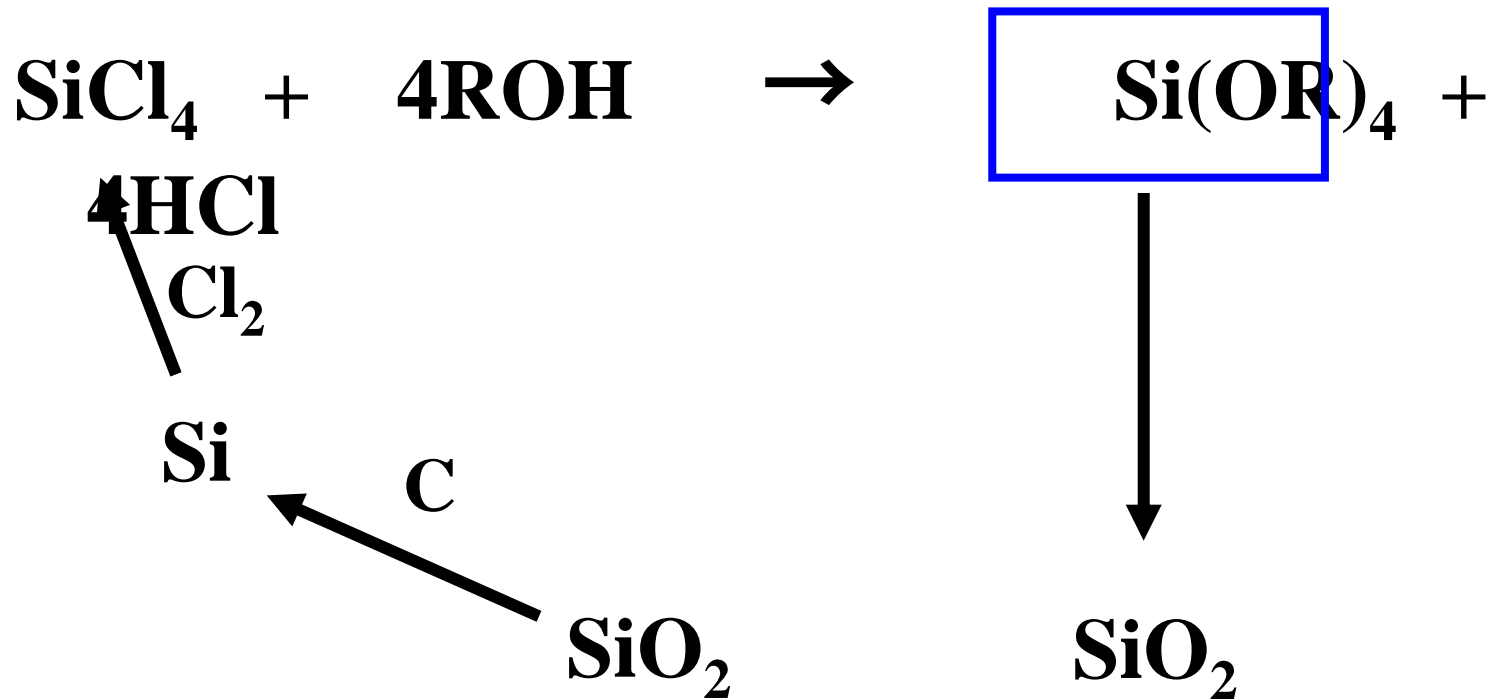
$\text{R} = \text{CH}_3$ (b.p. $121\text{ }^\circ\text{C}$),

C_2H_5 (b.p. $169\text{ }^\circ\text{C}$), etc.

Well defined monomeric SiO_4 unit

**Reactivity of alkoxy groups
(hydrolysis and condensation)**

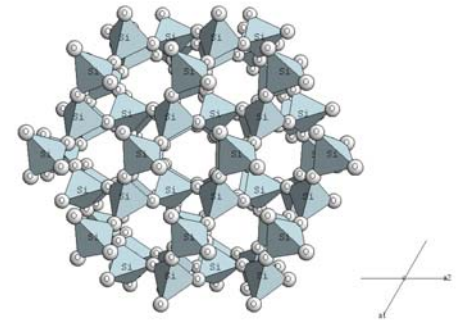
Synthesis of tetraalkoxysilane



Si-O system: from Lattice to Molecules

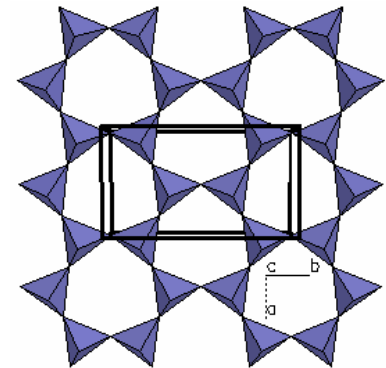
3D Lattice:

SiO_2 (Quartz, Cristobalite,....)
zeolites and mesoporous silica



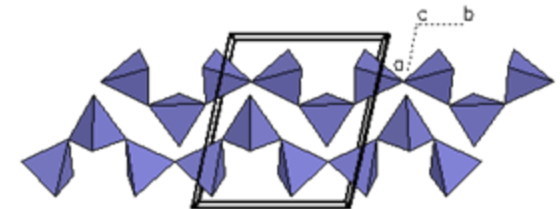
2D Lattice:

layered silicates (Mica, Kaolinite.....)



1D Lattice:

chain silicates (pyroxene,



Clusters

$\text{Si}_8\text{O}_{20}^{8-}$

Molecules:

$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(\text{OH})_4$

OUTLINE

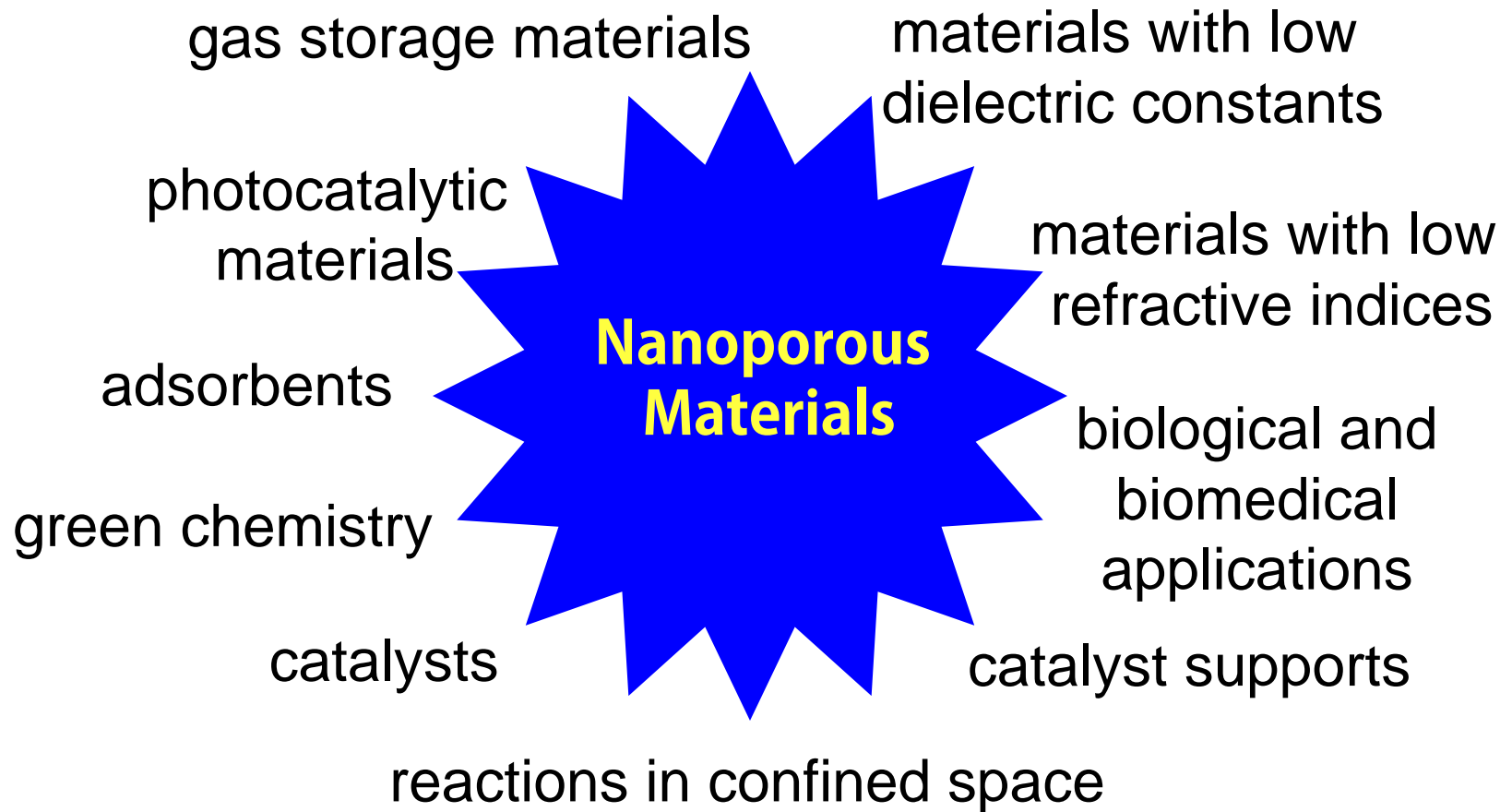
Background

Mesoporous materials

Mesoporous films utilizing alkoxysilanes

Design of alkoxysilanes and self-assembly

Varieties and possibilities

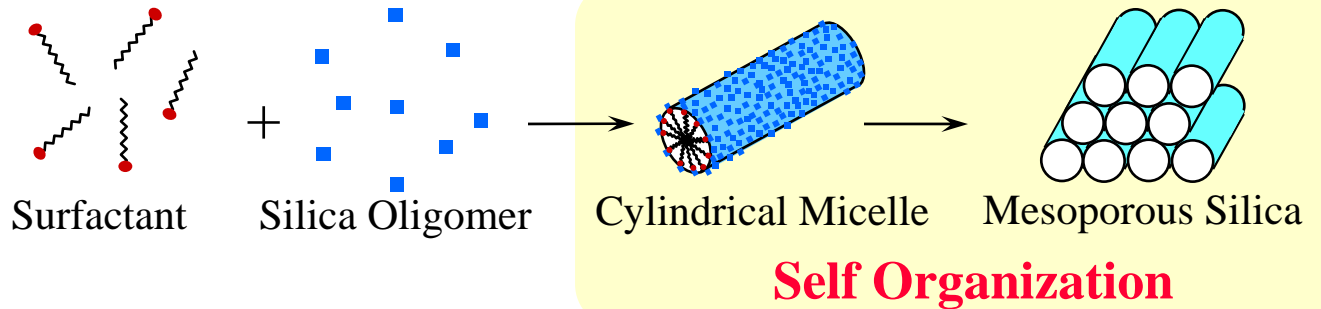


Design of Novel Porous Materials at a nanometer scale



Mesoporous Materials

*Regularly Arranged Mesopores (Pore: 2 ~ 50 nm)
Supramolecular Templating (Surfactant Micelles)*



100nm

1. Mesophases

2D-Hexagonal, 3D-Hexagonal, Cubic, Lamellar

2. Pore Sizes

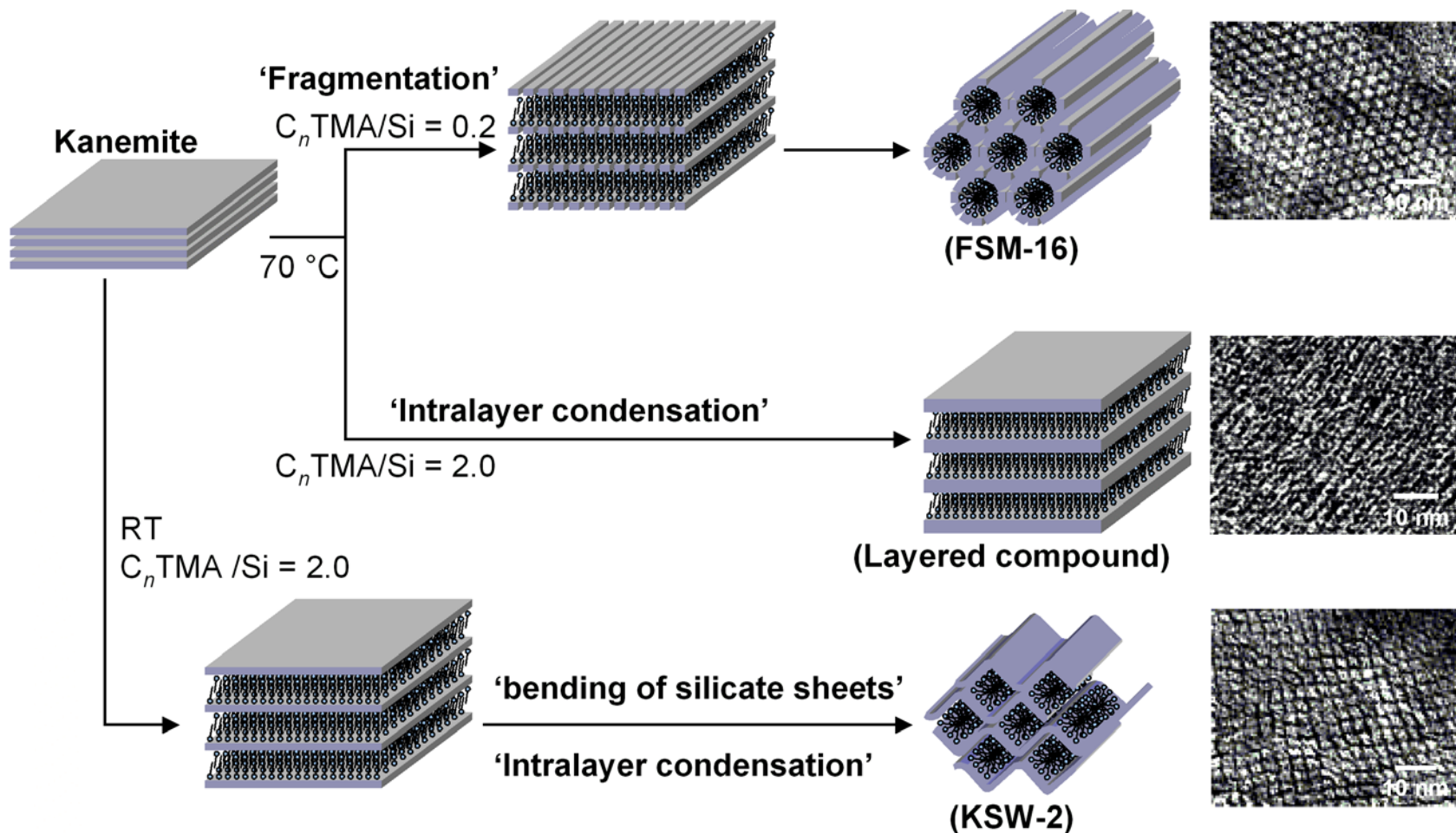
Alkyl Chain Length of Surfactant, Expander Molecules
Non-ionic Surfactants

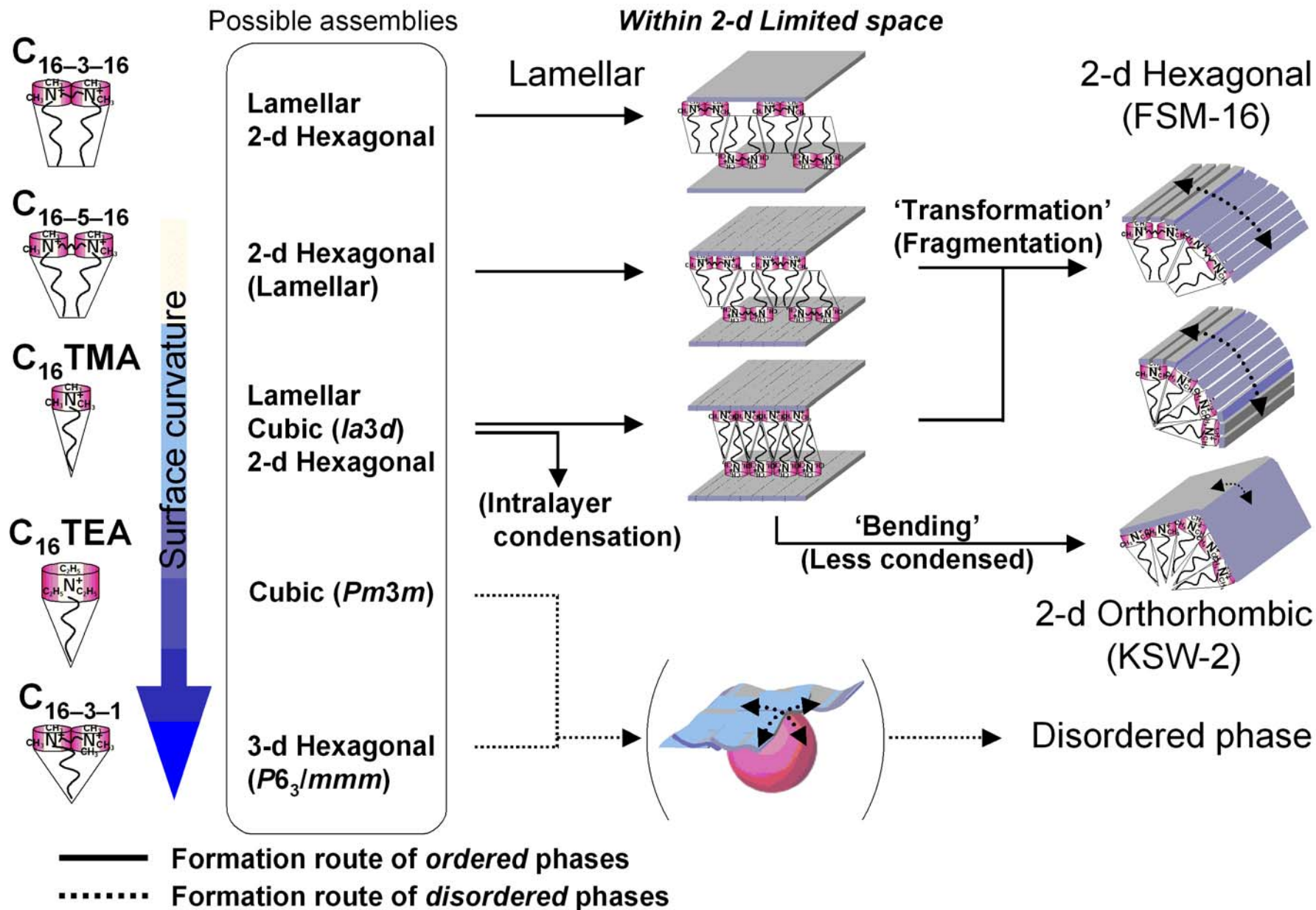
3. Wall Composites

Silica, Alumina, Titania, Zirconia, Hafnia, e.t.c.

4. Macroscopic Morphologies

Particle, Film, Sphere, Fiber, Monolith





Design of nanoporous materials

Porosity

Pore size, pore length, pore volume,
2D (orientation, uniaxial,...), 3D, Hierarchical
Ordered, Disordered
Straight pore, Cage-type pore, Chiral
Open pore and/or closed pore, Defects,.....
Pore surface/interface
“Entrance/Exit” and Outer surface
Static or Dynamic, Stimuli-responsive

Wall composition and structure

Metals, Oxides, Non-oxides, Organics,
Polymers, Metal complexes, Hybrids,
Supramolecules.....
Crystalline, Amorphous,..... , Density,.....

Morphology

Powders, Monodispersed Particles, Hollow
spheres, Monoliths, **Films**, Fibers,

Synthetic methods

Surfactants
Cooperative,
Lyotropic liquid
crystals,
Surfactant-free,
Magnetic field,
Substrate surface,
Phase transition,
.....

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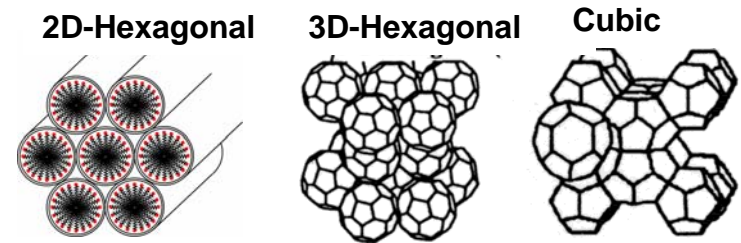
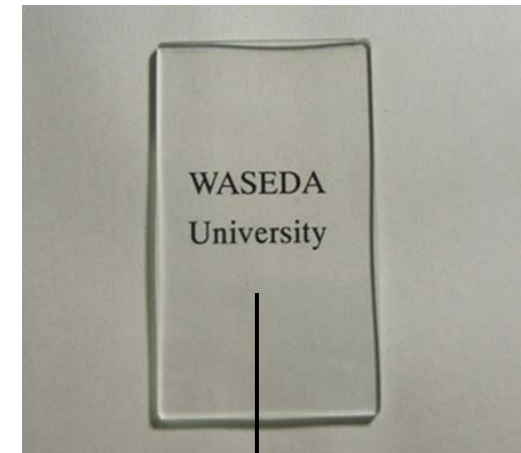
Varieties and possibilities

Mesoporous Films

- Homogeneous mesopores
- Large specific surface areas
- High transparency
- Various mesostructures
- Various chemical compositions
(Silica, Transition Metal Oxides,
Metals, Semiconductors, etc.)
- Controlled arrangements of
mesochannels and mesocages



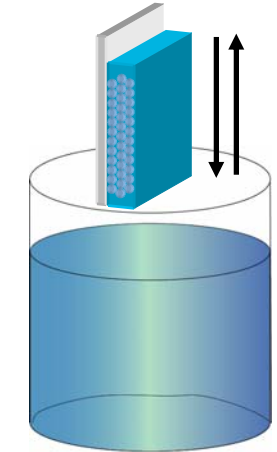
Optical, Electronic, and Molecular Devices,
Low-*k* Dielectrics, Photocatalysts, Sensors,
Biomedical, ...



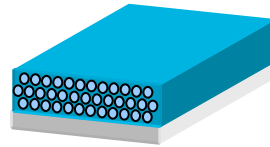
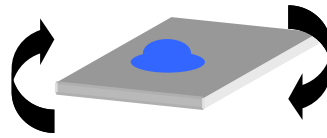
Various Mesostructures

Synthetic methods

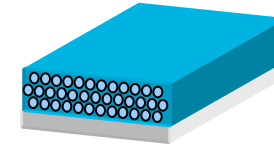
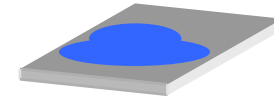
■ EISA (Evaporation Induced Self-Assembly)



Dip-Coating



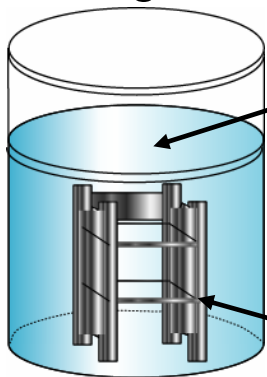
Spin-Coating



Casting

■ Hydrothermal Synthesis

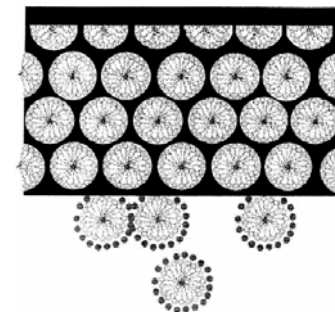
(Heterogeneous Nucleation and Growth)



Air-Water Interface

Solid-Water Interface

Model^a

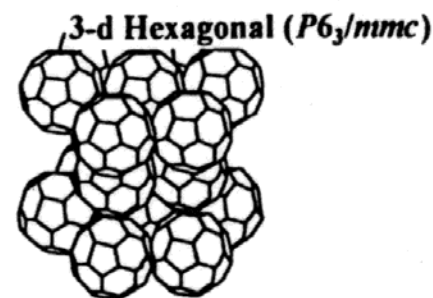
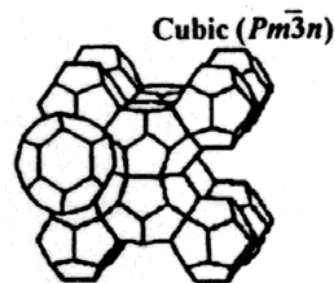
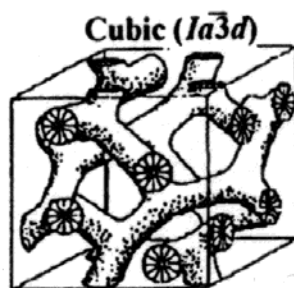
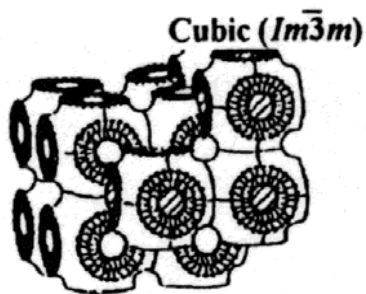


a) H. Yang, G. A. Ozin, *Nature*, 1996, 379, 703.

Mesoporous Silica Films

Various Mesostructures, Conditions

- $Pm\bar{3}n$, $Im\bar{3}m$ (P123^a, F127^a, CTEABr^b)
- Lamellar (SDS^c, Anionic Surfactant)
- $P6_3/mmc$ (CTAB^{d,e})
- $Ia\bar{3}d$ (Brij56^f)
- $R3m$ (P123^g)
- $p6mm$ (Basic Condition^h)



a) Zhao, D., Stucky, G. D., *Adv.Mater.*, **1998**, 10, 1380.

b) Zhao, D., Stucky, G. D., *Chem. Commun.*, **1998**, 2499.

c) Huang, M. H., Zink, J. I., *Langmuir*, **1998**, 14, 7331

d) Besson, S., Boilot, J.-P., *J. Phys Chem. B* **2000**, 104, 12093.

e) Grosso, D., Babonneau, F., *J. Mater. Chem.*, **2000**, 10, 2085.

f) Hayward, R. C., Chmelka, B. F., *Langmuir*, **2004**, 20, 5998.

g) Eggiman, B. W., Hillhouse, H. W., *Chem. Mater.*, **2006**, 18, 723.

h) Park, S. S., Ha, C.-S. *Chem.Commun.*, **2004**, 1986.

Mesoporous Silica Film (Hydrothermal)

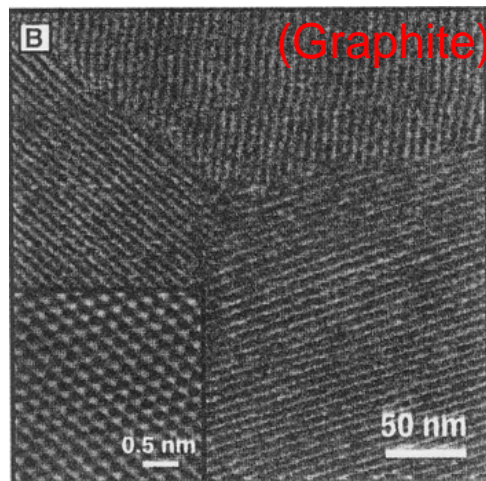
■ Hydrothermal Synthesis

(On Mica, Graphite & Air-Water Interface, 2D-Hexagonal)

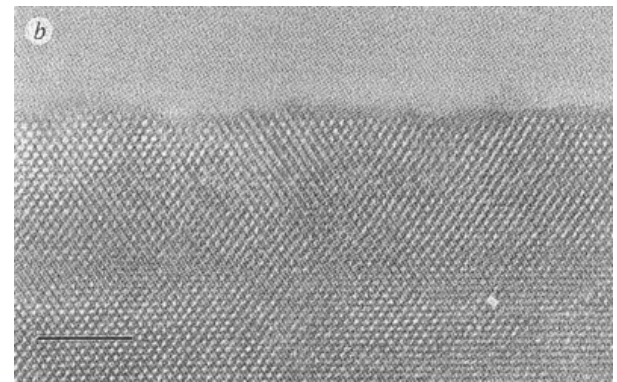
SEM^a



AFM^c



TEM^a



- Highly Ordered 2D-Hexagonal Mesoporous Structure
- Alignment Control of Mesochannels Reflected the Symmetry of Substrates

a) H. Yang, G. A. Ozin, *Nature*, **1996**, 379, 703.

b) H. Yang, G. A. Ozin, *J.Mater.Chem.*, **1997**, 7, 1755

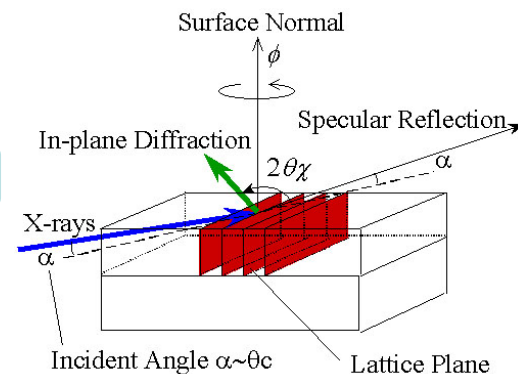
c) I. A. Aksay, et al., *Science*, **1996**, 273, 892.

d) H. Yang, G. A. Ozin, *Nature*, **1996**, 381, 589.

Characterization

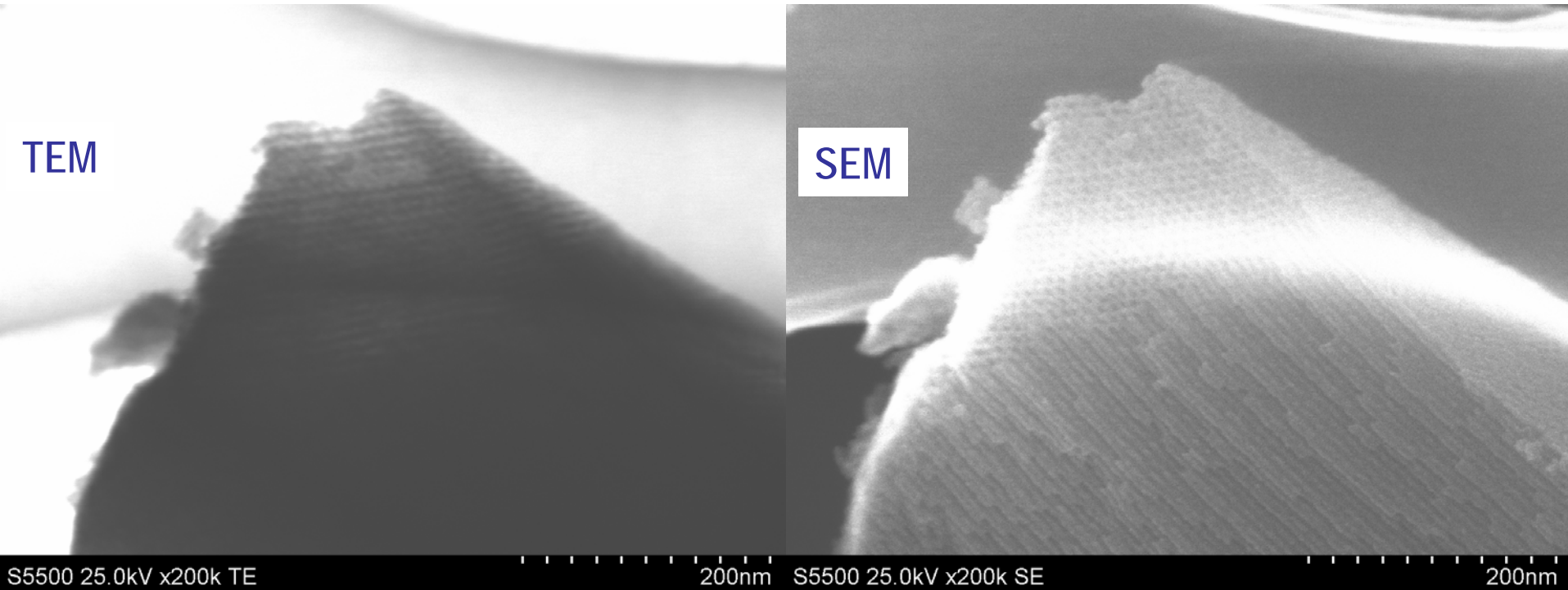
- X-Ray Diffraction (Out-Of-Plane, In-Plane, 2-Dimensional^l)
- *In-Situ* Time-Resolved Small Angle X-Ray Scattering^{a-f}
- Small Angle Neutron Scatteringⁱ
- High Resolution Scanning Electron Microscopy (HR-SEM)^{g,h}
- Transmission Electron Microscopy (TEM)
- Gas Adsorption
- Secular X-Ray Refractivity
- Positron Annihilation
- Ellipsometry
- etc....

In-Plane XRD



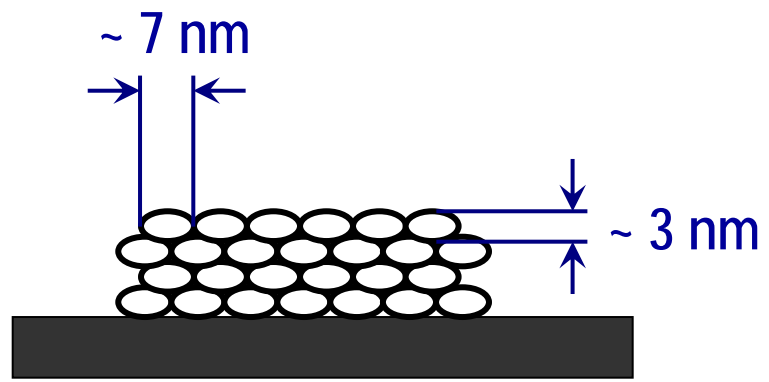
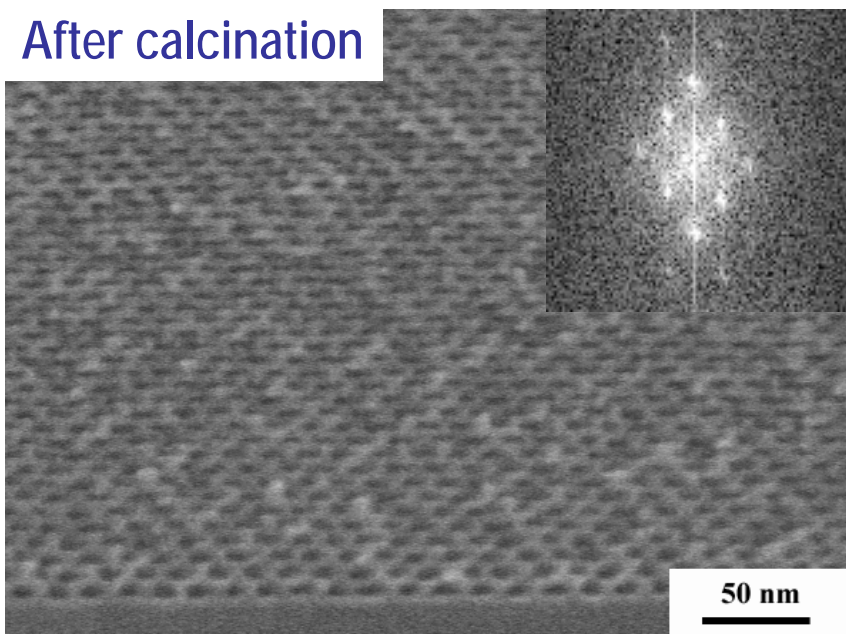
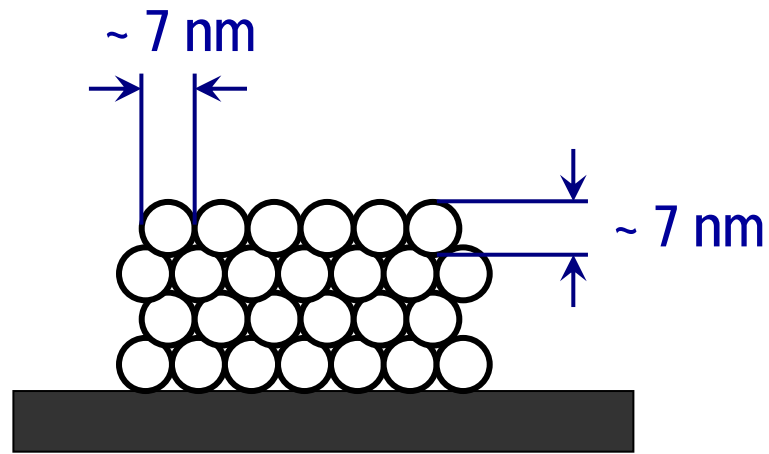
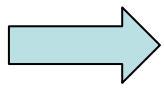
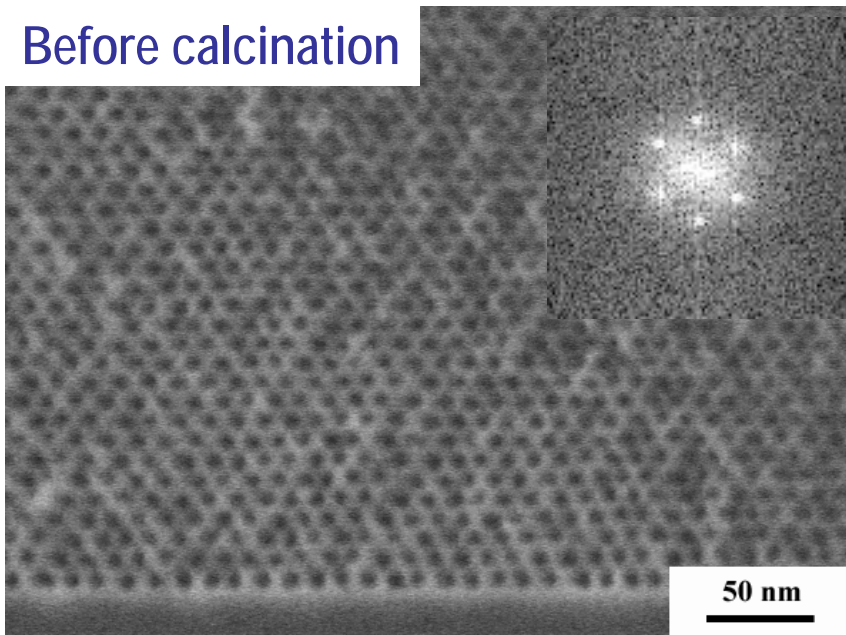
- a) Grosso, D., Babonneau, F., *Chem. Mater.*, **2001**, 13, 1848.
b) Grosso, D., Amenitsch, H., *Chem. Comm.*, **2002**, 748.
c) Doshi, D. A., Brinker, C. J., *J. Am. Chem. Soc.*, **2003**, 125, 11646.
d) Doshi, D. A., Brinker, C. J., *J. Phys. Chem. B* **2003**, 107, 7683.
e) Cagnol, F., Sanchez, C., *J. Mater. Chem.*, **2003**, 13, 61.
f) Falcaro, P., Innocenzi, P., *J. Am. Chem. Soc.*, **2005**, 127, 3838.
g) Miyata, H.; Kuroda, K., *Adv. Mater.*, **1999**, 11, 857.
h) Wu, C.-H., Kuroda, K. *J. Mater. Chem.*, **2006**, 16, 3091.
l) Vogt, B. D., Watkins, J. J., *Chem. Mater.*, **2005**, 17, 1398.
j) Noma, T., Iida, A., *Nuclear Inst. Methods Phys. Research A* **2001**, 467–468, 1021.

SEM and TEM images for the same mesostructure



The TEM and SEM image of the same 2D hexagonal mesostructure were taken ((a) and (b), respectively) at the same position. The SEM image shows a solid picture of the sample and obviously present a clear mesostructure on the external surface of the sample, while the structure can not be observed by TEM.

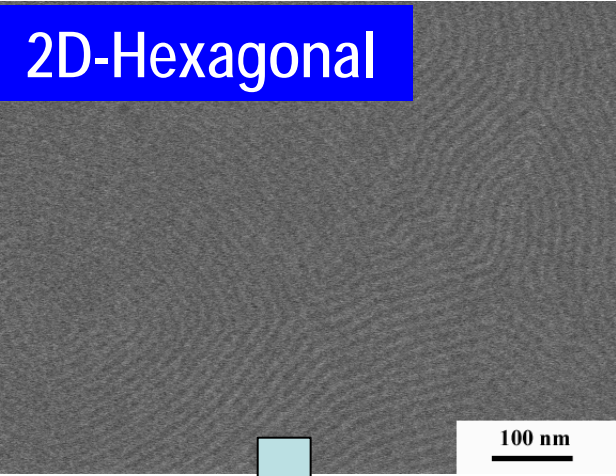
Results: Influence of Calcination on the Surface Morphology



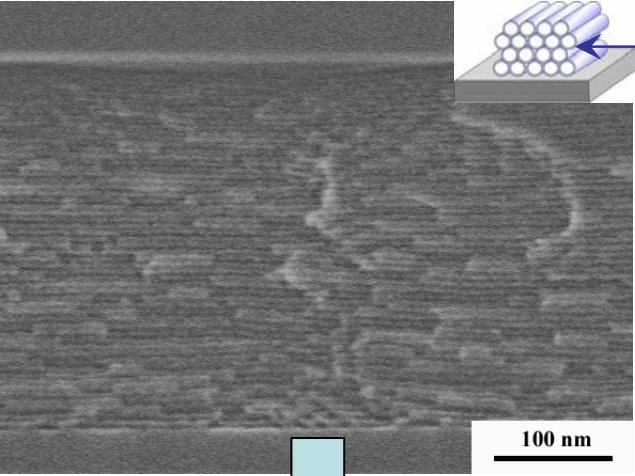
■ Anisotropic contraction occurred in the direction perpendicular to the substrate upon calcination

Results: Pt Nanowire Thin Films Replicated from 2D hexagonal SiO₂ films

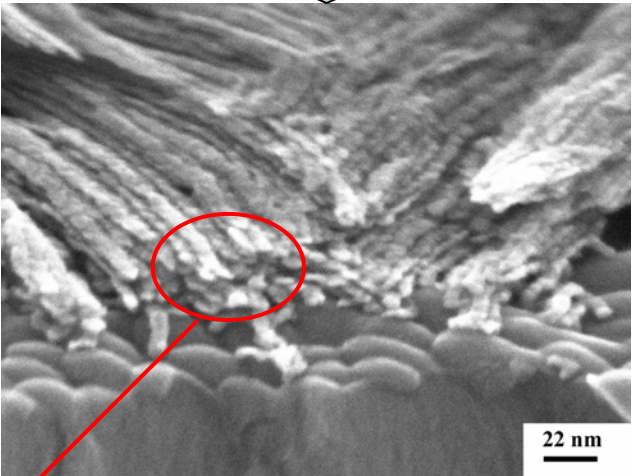
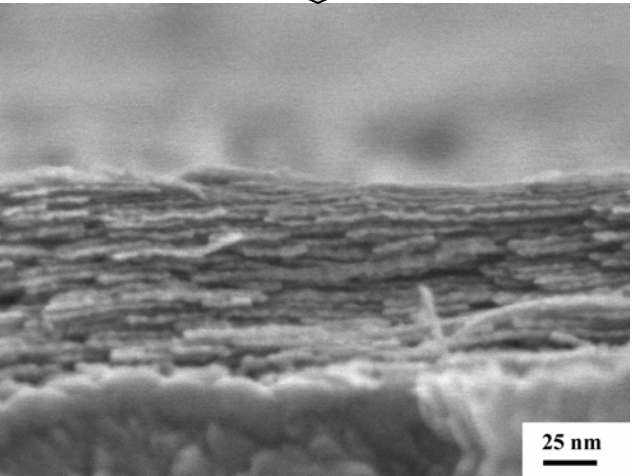
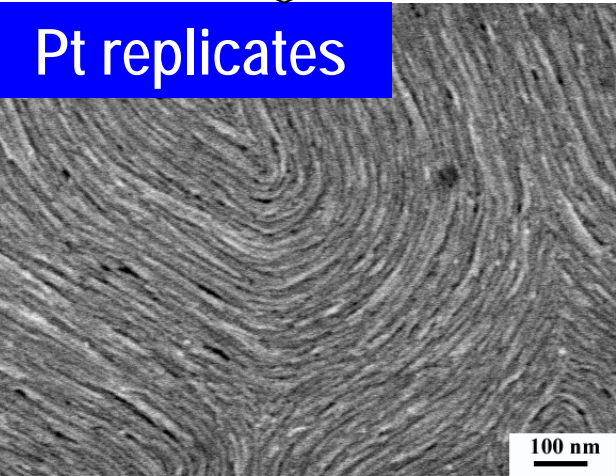
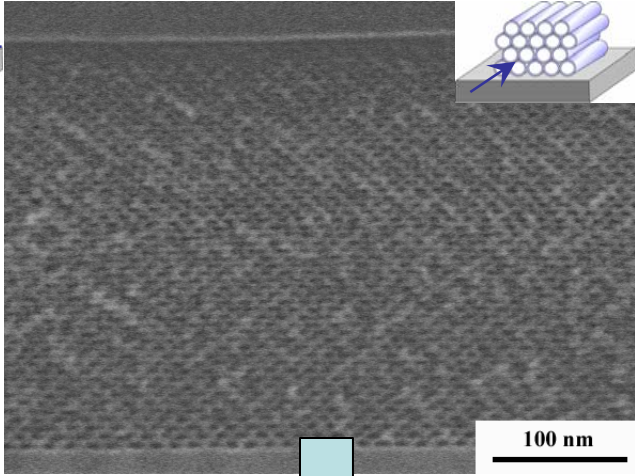
Top view



Cross-sectional view



Cross-sectional view



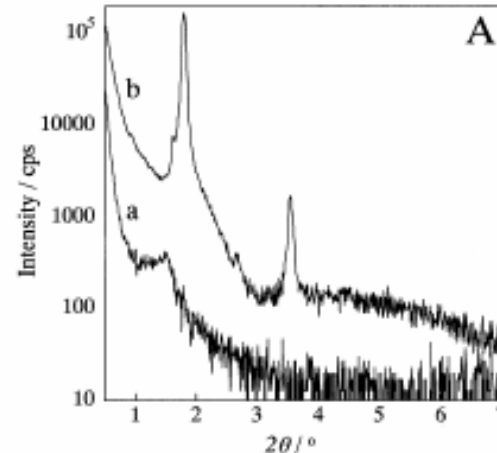
■ Pt nanowires with ellipsoidal cross section

Chia-Wen Wu et al., *J. Mater. Chem.* (2006)

Mesostructured SnO₂ Film

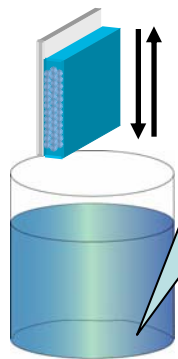
Mesostructured SnO₂ Film

- Transparent Semiconductor (NESA)
- Highly Transparent
- Gas Sensing Property



a: Without Water Vapor Treatment
b: After Water Vapor Treatment

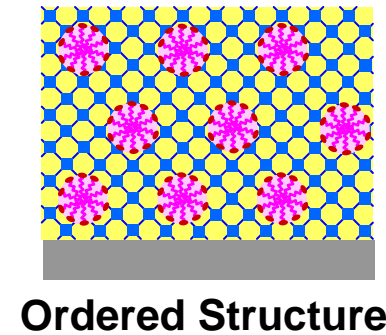
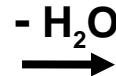
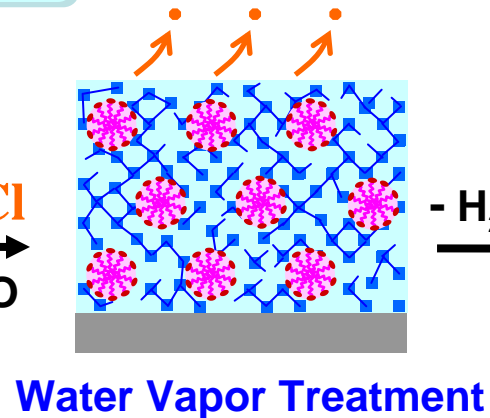
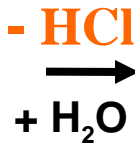
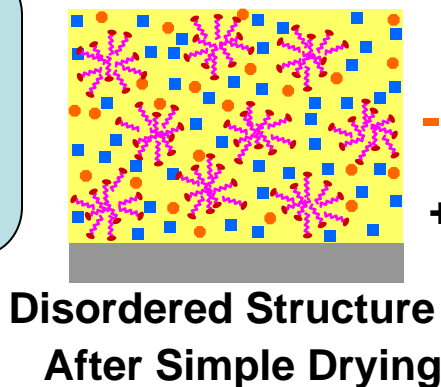
Method



Brij76 or
Brij58
H₂O
SnCl₄
EtOH

Dip-Coating

Formation Process

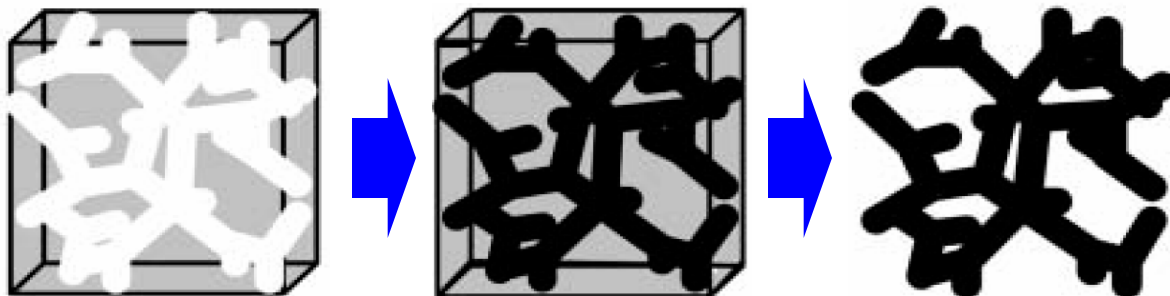


Synthesis Methods for Mesoporous Metals

Replication Method (proposed by R. Ryoo et al.)

Chemical Reduction

HF Etching



- Hard-templates
- Noble metals
- Two-step processes

C. H. Ko et al., *Chem. Commun.*, 2467 (1996).

Direct Physical Casting (proposed by G. S. Attard et al.)

Nano-Electrodeposition

Removal of Template



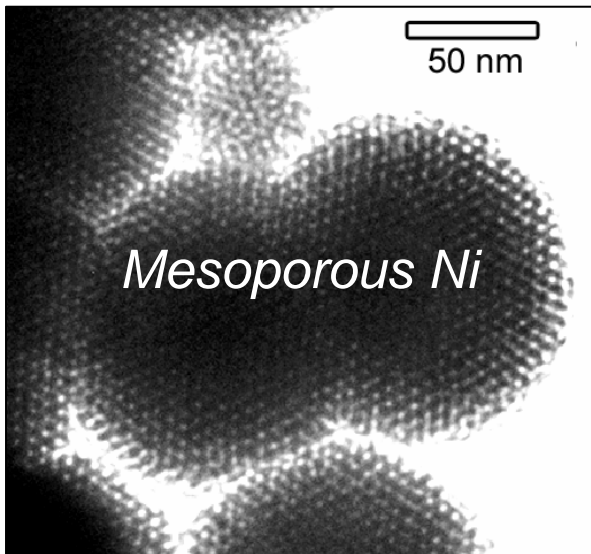
- Soft-templates
- Various metals
- One-pot process

Attard et al., *Angew. Chem. Int. Ed.*, 33, 1315 (1997).

Our previous study

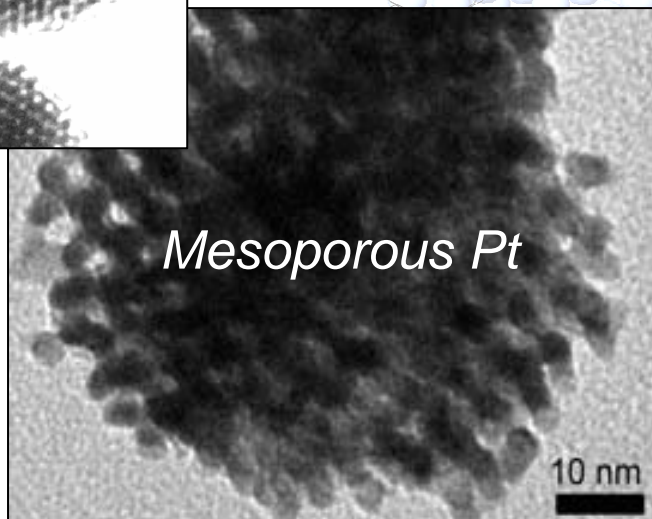
~Toward highly ordered mesoporous metals and alloys~

Finely controlled metallization



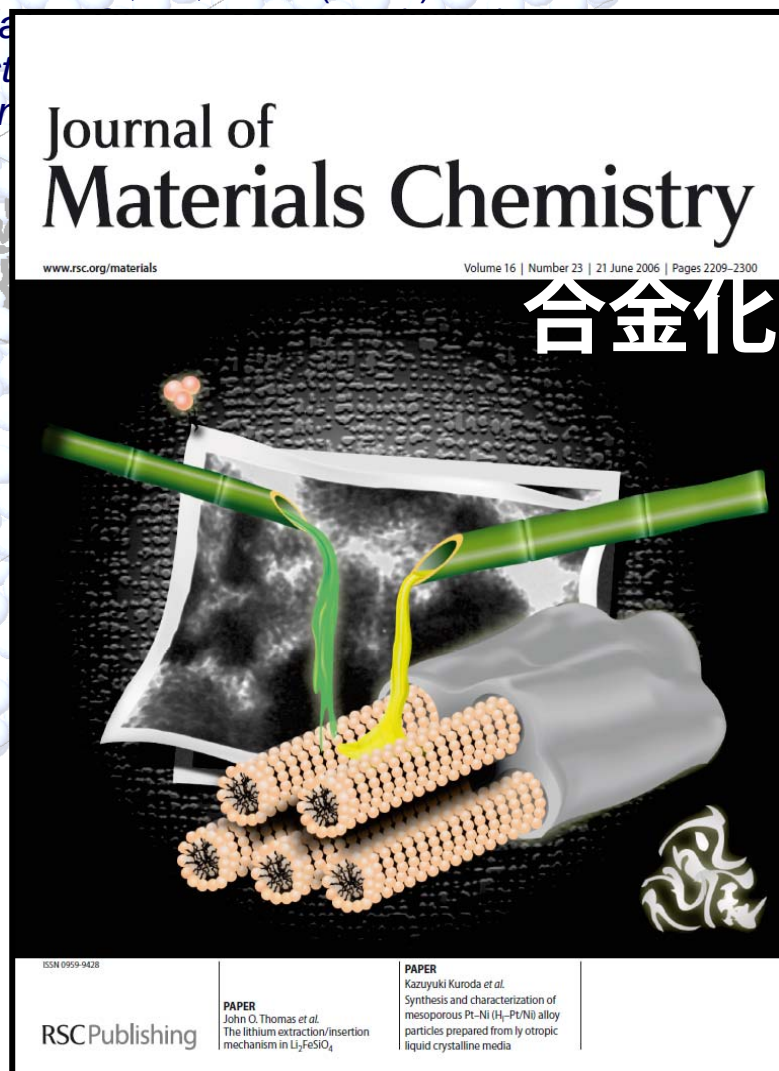
Y. Yamauchi *et al.*, *Chem. Lett.*, **33**, 542 (2004).
Chem. Lett., **33**, 1576 (2004).

J. Mater. Chem.
Electrochim. Acta
Chem. Commun.

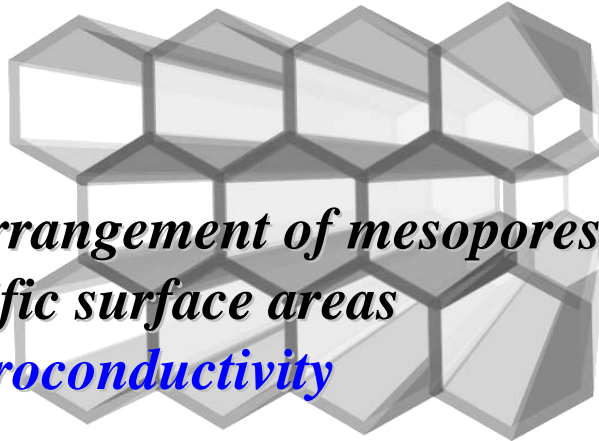


Structural characterization

Y. Yamauchi *et al.*, *J. Mater. Chem.*, **14**, 2935 (2004).
Stud. Surf. Sci. Catal., **156**, 457 (2005).
J. Mater. Chem., **16**, 2229 (2006).



Mesoporous Metals *toward Nanostructured Catalysts*



Periodic arrangement of mesopores
High specific surface areas
High electroconductivity

Synthesis ▶

Highly ordered mesostructure
Structural resolution
Alloying in pore wall

Development of New Approach for Microfabrication

Novel Applications

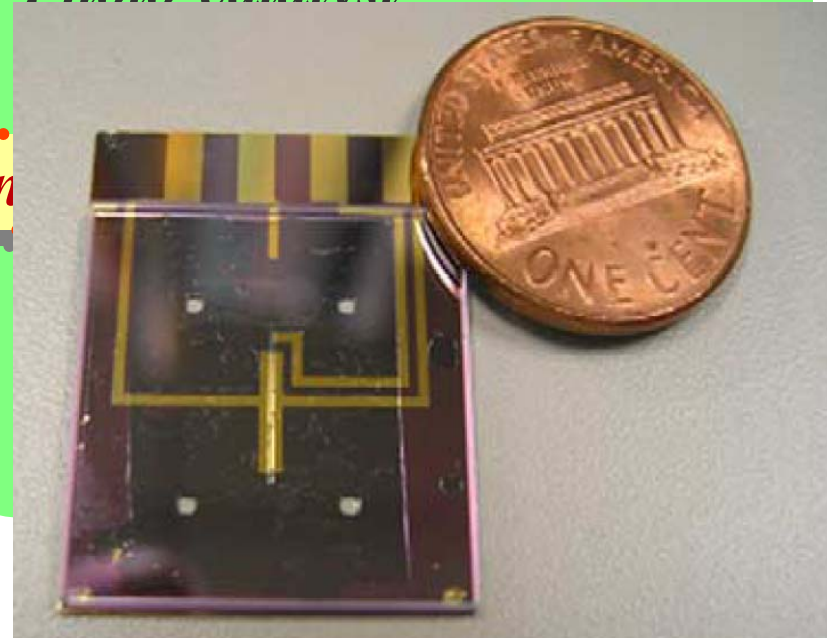
Micro-sensors, Micro-batteries,
Micro-bioactive materials, Miniaturized devices, etc...

Environmental Catalysts

- *NO_x removal catalyst*
- *Photo-catalyst*
-

En

-
-
-

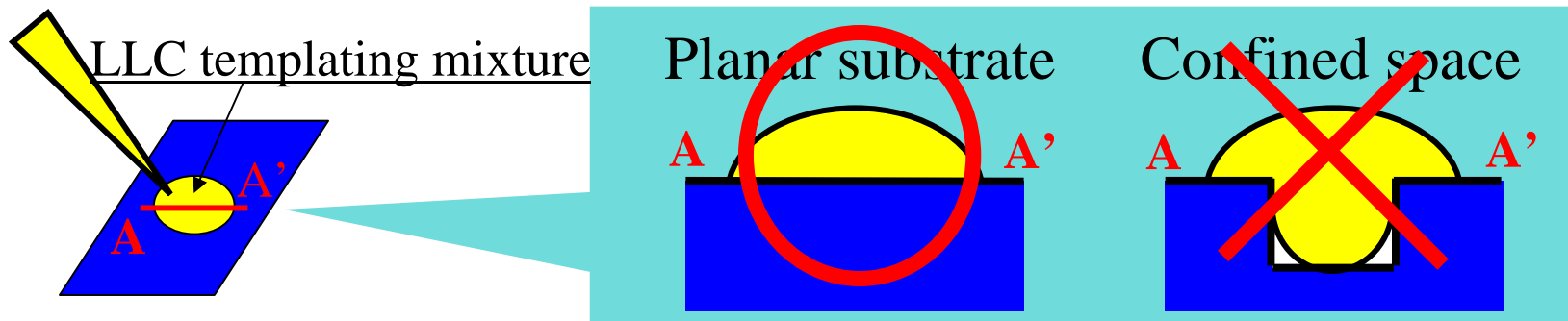
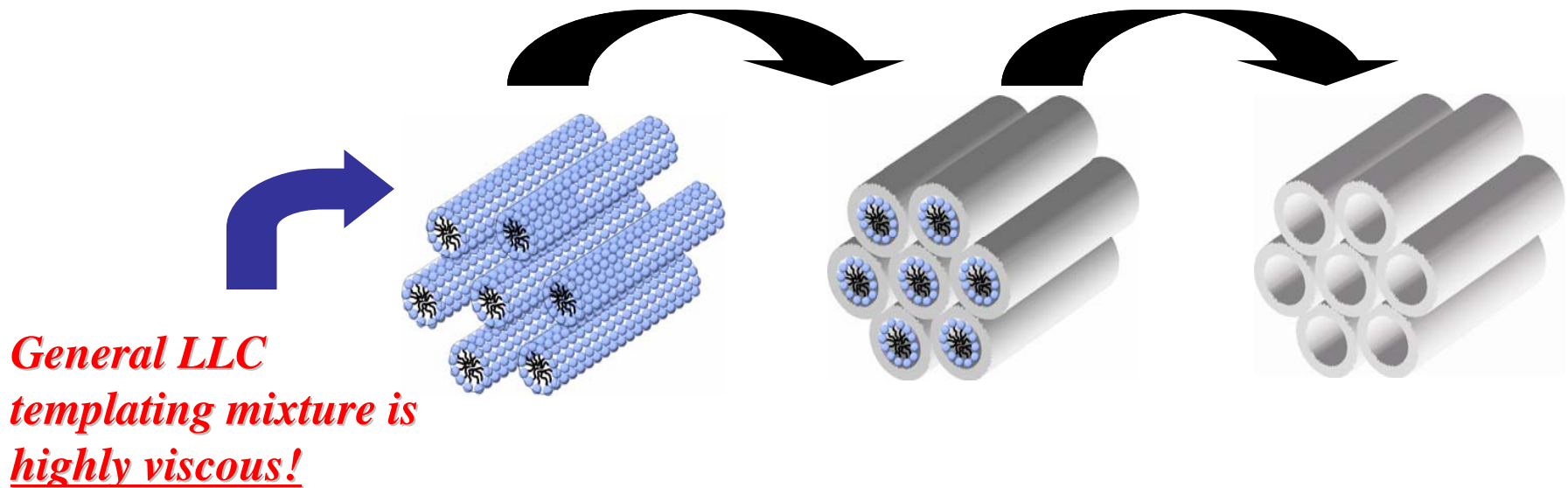


Microfabrication of Mesoporous Metals

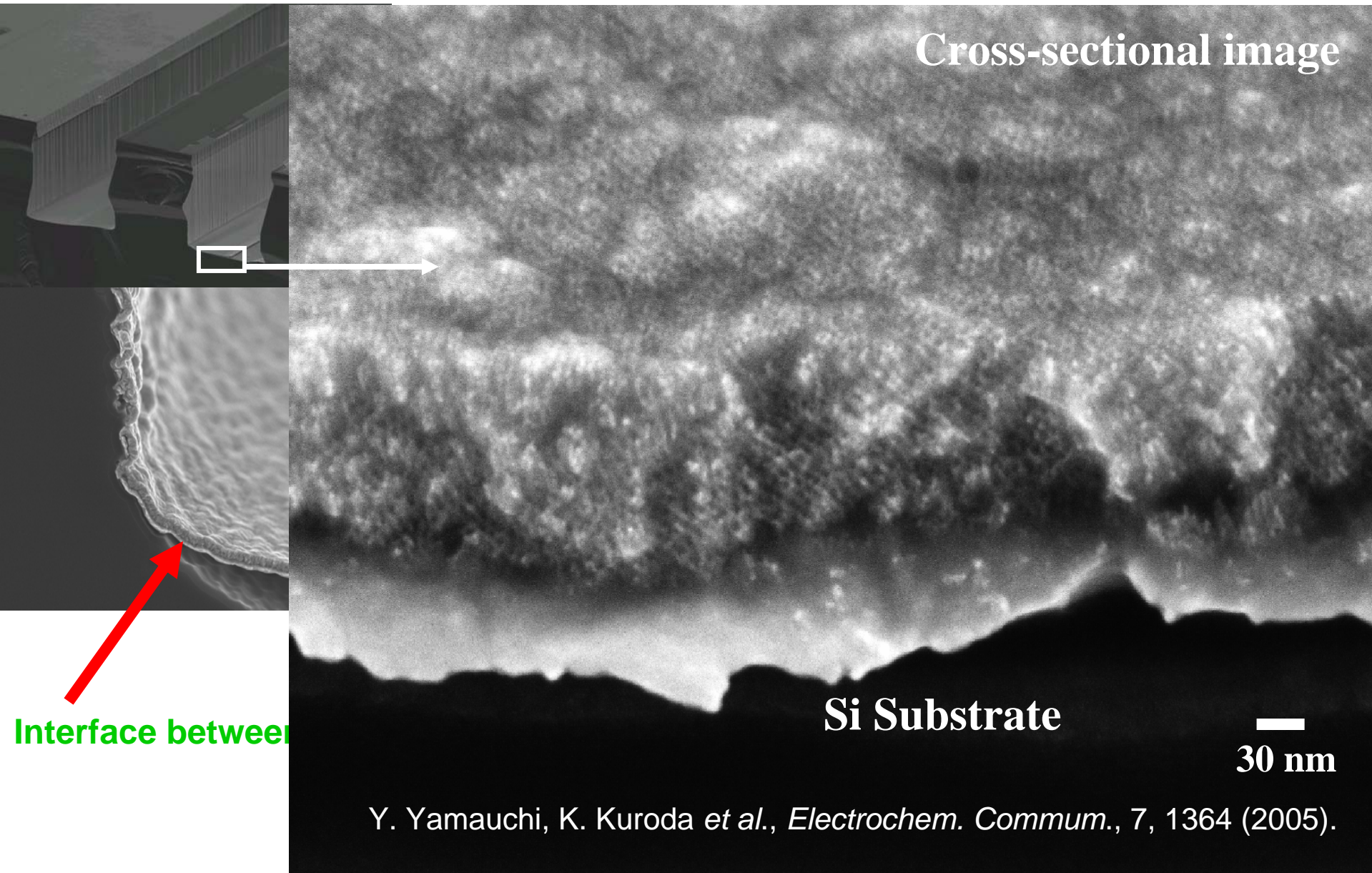
-For the integration of multifunctions and the enhancement of functional activity-

Novel Applications

micro-sensors, micro-batteries,
micro-bioactive materials, miniaturized devices, etc...

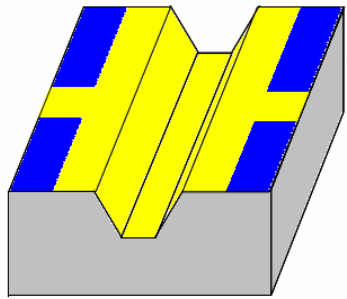


Bottom Surface in Microchannel

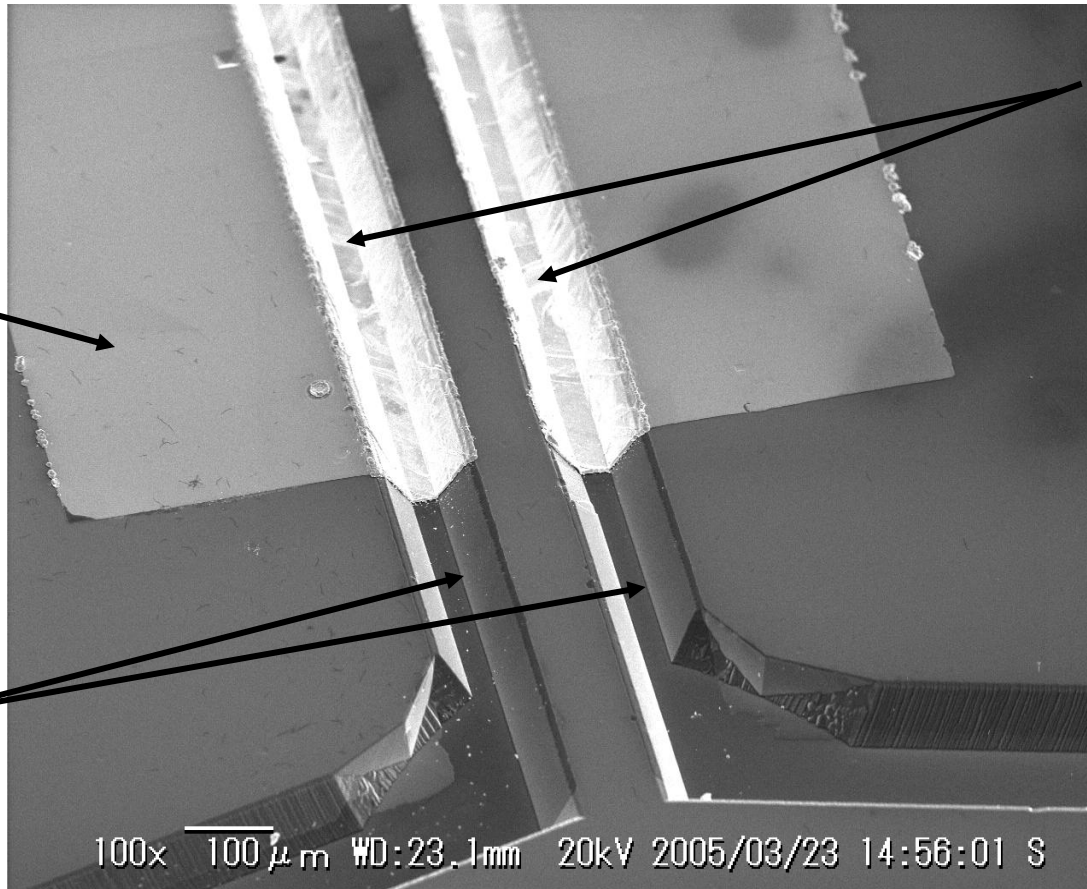


Y. Yamauchi, K. Kuroda *et al.*, *Electrochem. Commun.*, 7, 1364 (2005).

SEM Observation



Au/Ti/SiO₂



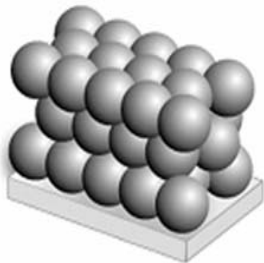
Mesoporous Pt

Microchannels

Successful deposition of mesoporous Pt only inside microchannels

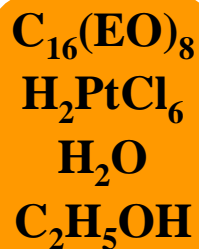
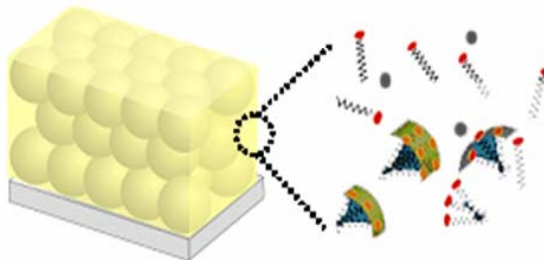
Experimental procedure for Hierarchical porous electrode

(i) Colloidal crystals

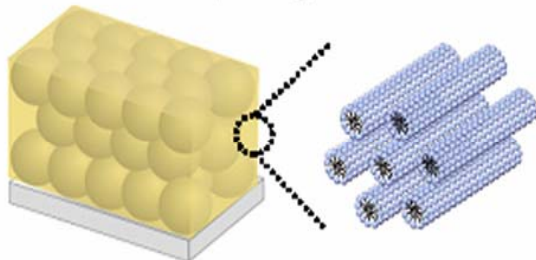


Polystyrene spheres (460 nm) were assembled onto a Au-coated Si substrate by a dip-coating method (500 nm/s).

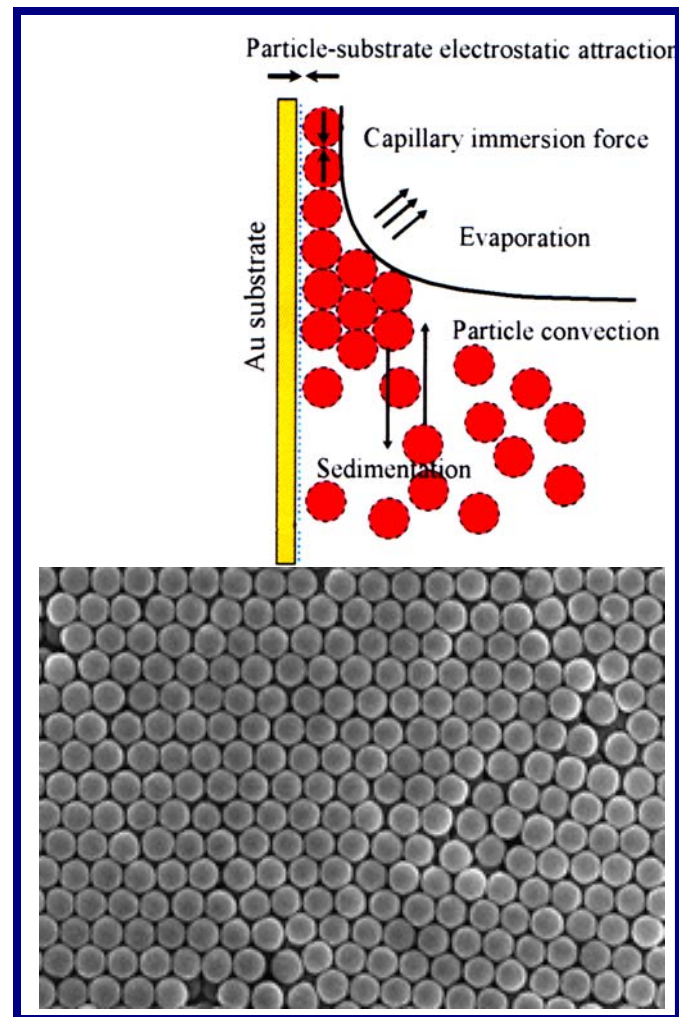
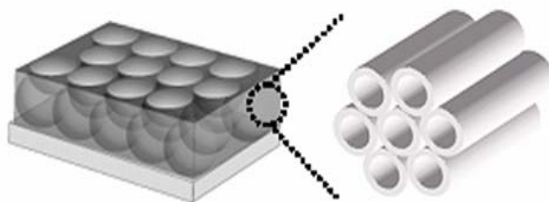
(ii) Immersion of LLC former



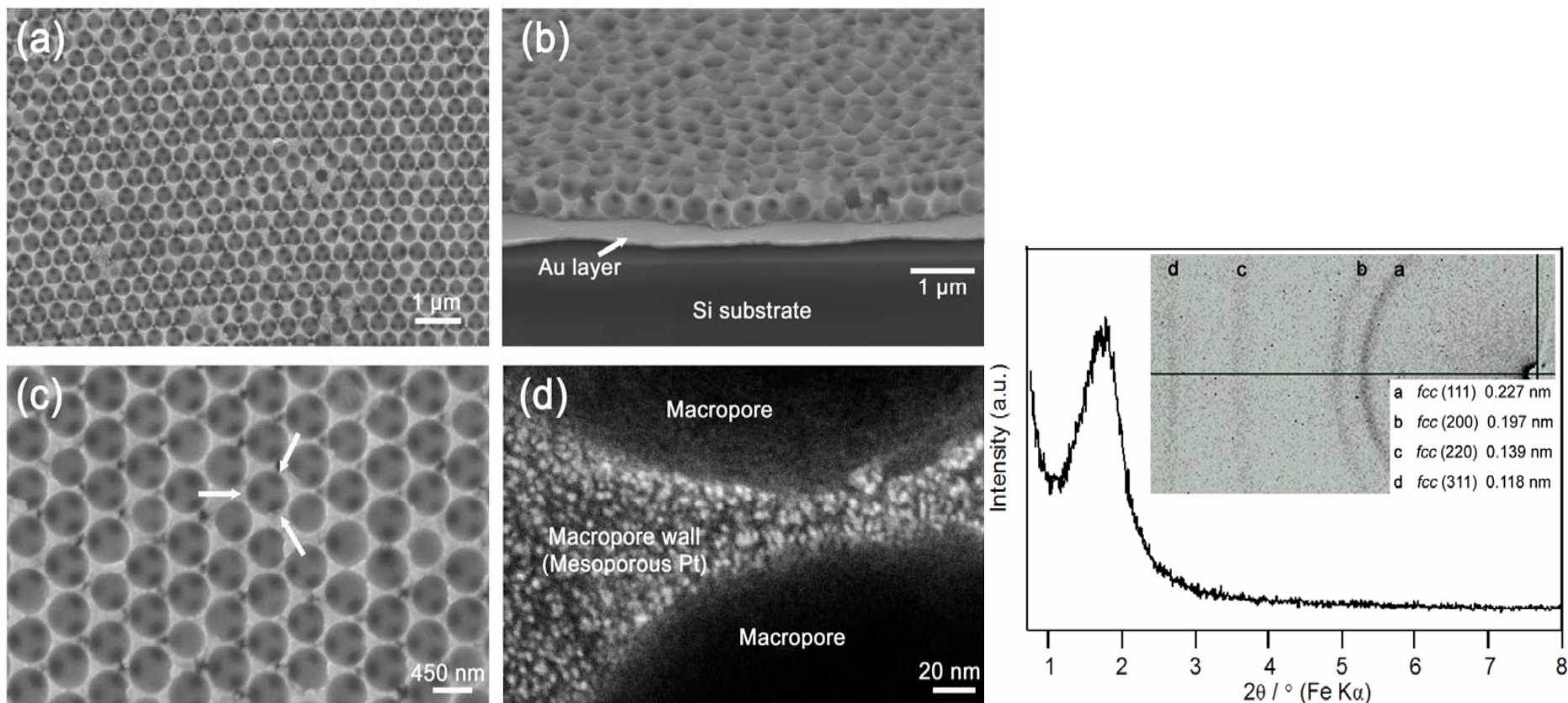
(iii) Formation of LLC templating mixture



(iv) Pt deposition & Removal of templates



Hierarchical porous Pt electrode



The three windows, as indicated with arrows, correspond to the interconnection of three neighboring macropores located below the macropores observed in the image.

The macropore wall consists of small nanoparticles (around 3 nm in average diameter). These nanoparticles are interconnected to create mesoporosity.

Structural control of mesoporous silica films

■ Alignment Control

- **Uniaxially aligned mesochannels**

Anisotropic properties by incorporating various guest species

- **Single-Crystalline Mesoporous Structure**

Three-dimensional arrays of nano"crystals"

- **Perpendicular Orientation**

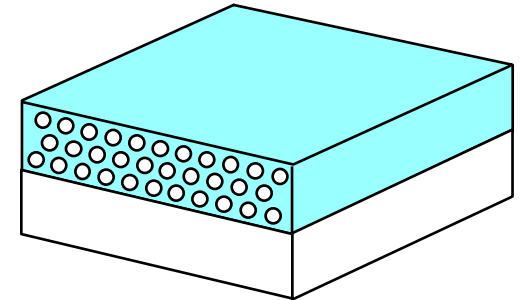
High accessibility from film surface to substrate

Alignment Controlled Mesochannels

■ Uniaxially Aligned Mesochannels

Methods

- Crystalline Substrates
(Mica, Graphite, Si(110)^a)
- External Fields
(Magnetic^b, Electronic^c, Flow^d...)
- Substrates with Surface Structural Anisotropy
(Rubbing Method^e, Photo-Orientation^f, Guided Growth^c, LB Film...)

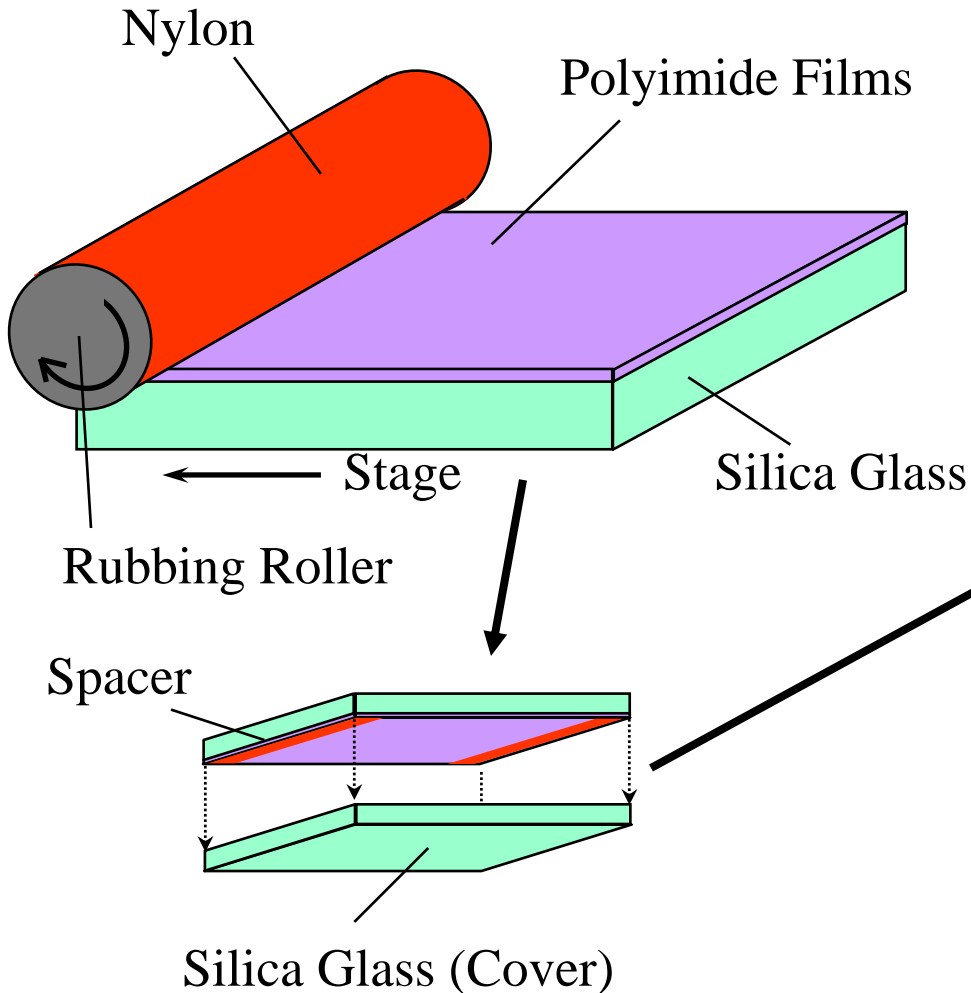


- a) Miyata, H., Kuroda, K. *J. Am. Chem. Soc.* **1999**, 121, 7618.
b) Tolbert, S.H., Chmelka, F., *Science*, **1997**, 278, 264.
Yamauchi, Y., Kuroda, K., *J. Mater. Chem.*, **2005**, 15, 1137.
c) Trau, M., Aksay, I.A. *Nature*, **1997**, 390,674.
d) Hillhouse, H. W., Tsapatsis, M. *Chem. Mater.* **1997**, 9, 1505.
e) Miyata, H., Kuroda, K. *Chem. Mater.* **1999**, 11, 1609.
Miyata, H., Kuroda, K. *Chem. Mater.* **2000**, 12, 49.
Miyata, H., Kuroda, K. *Chem. Mater.* **2002**, 14, 766.
f) Kawashima, Y., Ichimura, K. *Chem. Mater.* **2002**, 14, 2842.
Fukumoto, H., Seki, T. *Adv. Mater.* **2005**, 17, 1035.

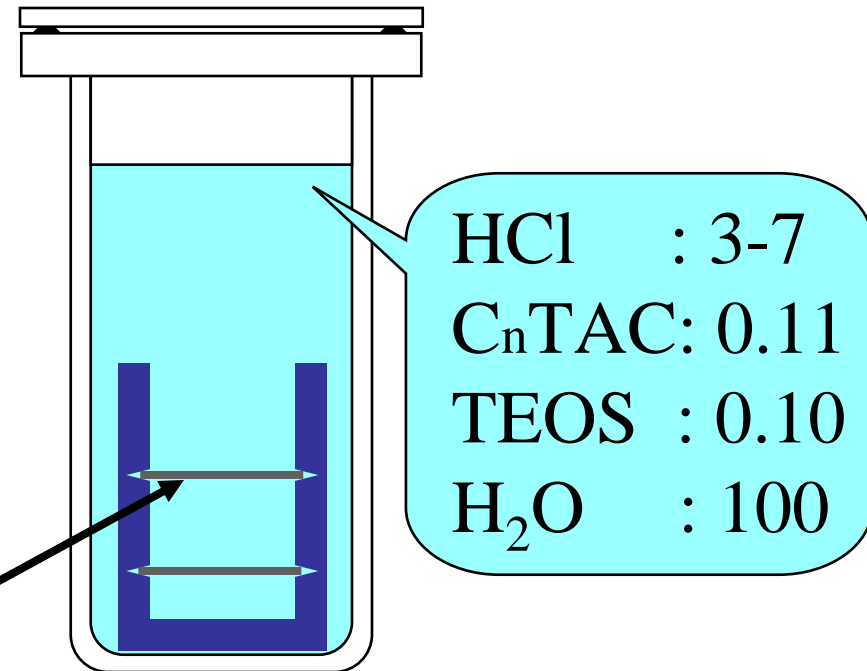


Preparation of the Aligned Mesoporous Silica

Rubbing Treatment



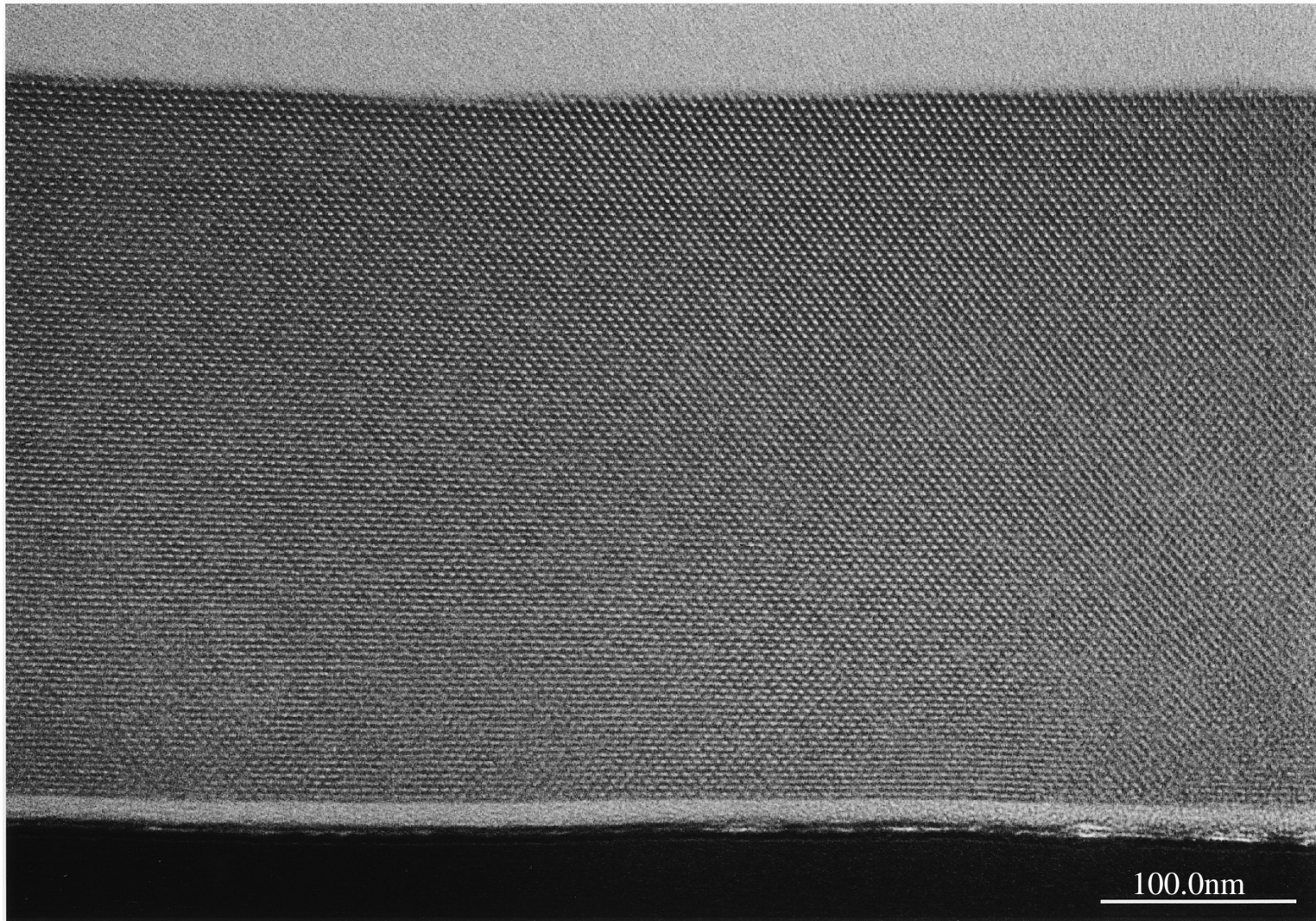
Preparation



80°C 1 week

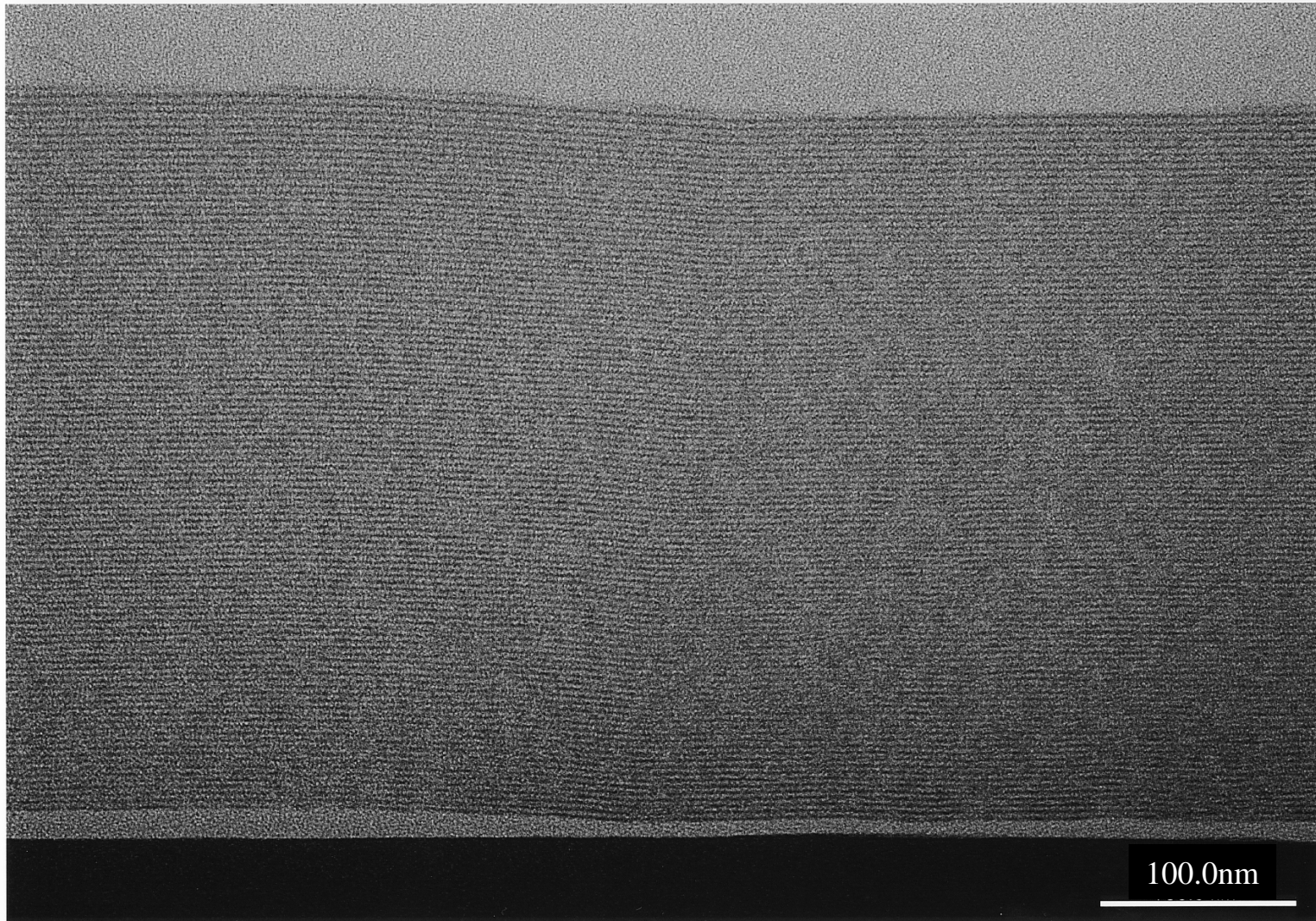
Cross-sectional TEM of the MPS on the PI-2 Film

Sliced Parallel to the Rubbing Direction



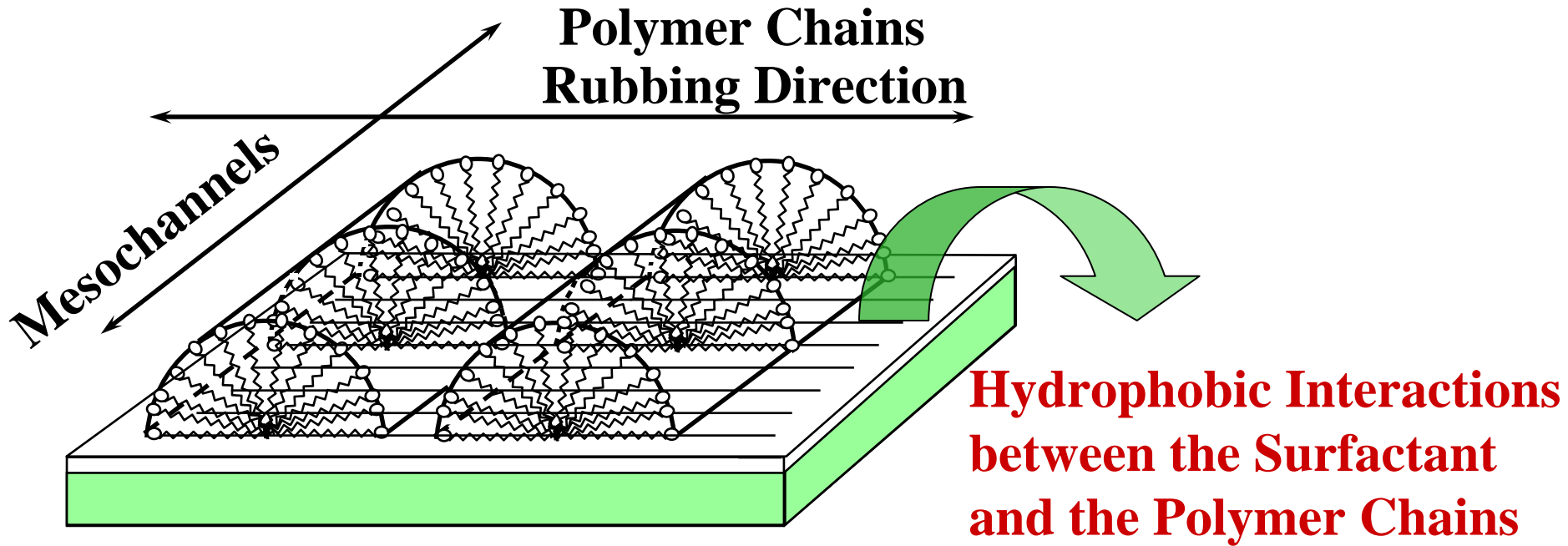
Cross-sectional TEM of the MPS on the PI-2 Film

Sliced Normal to the Rubbing Direction



Alignment Mechanism

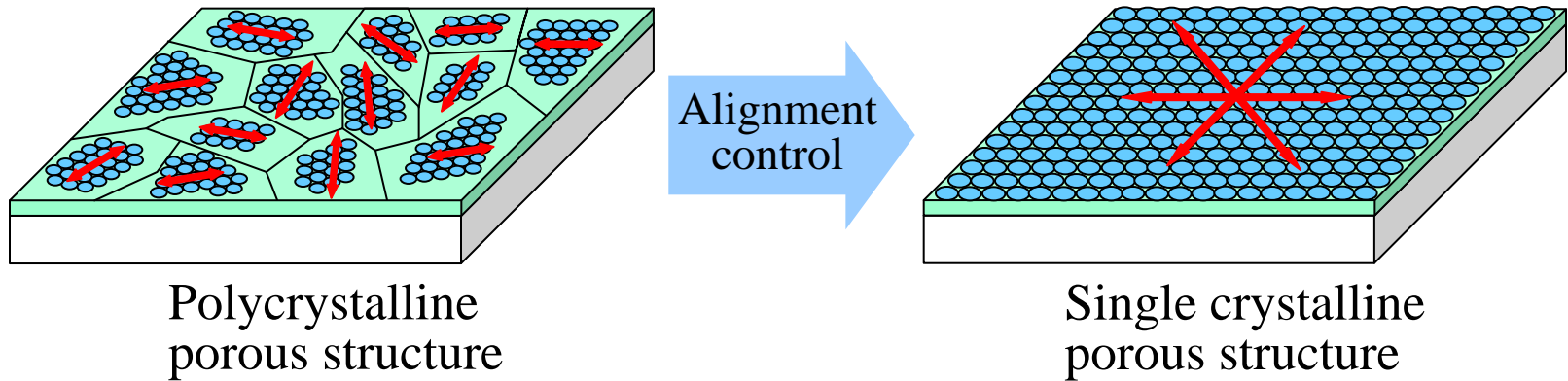
Alignment Model on the Rubbing-treated PI-2 Film

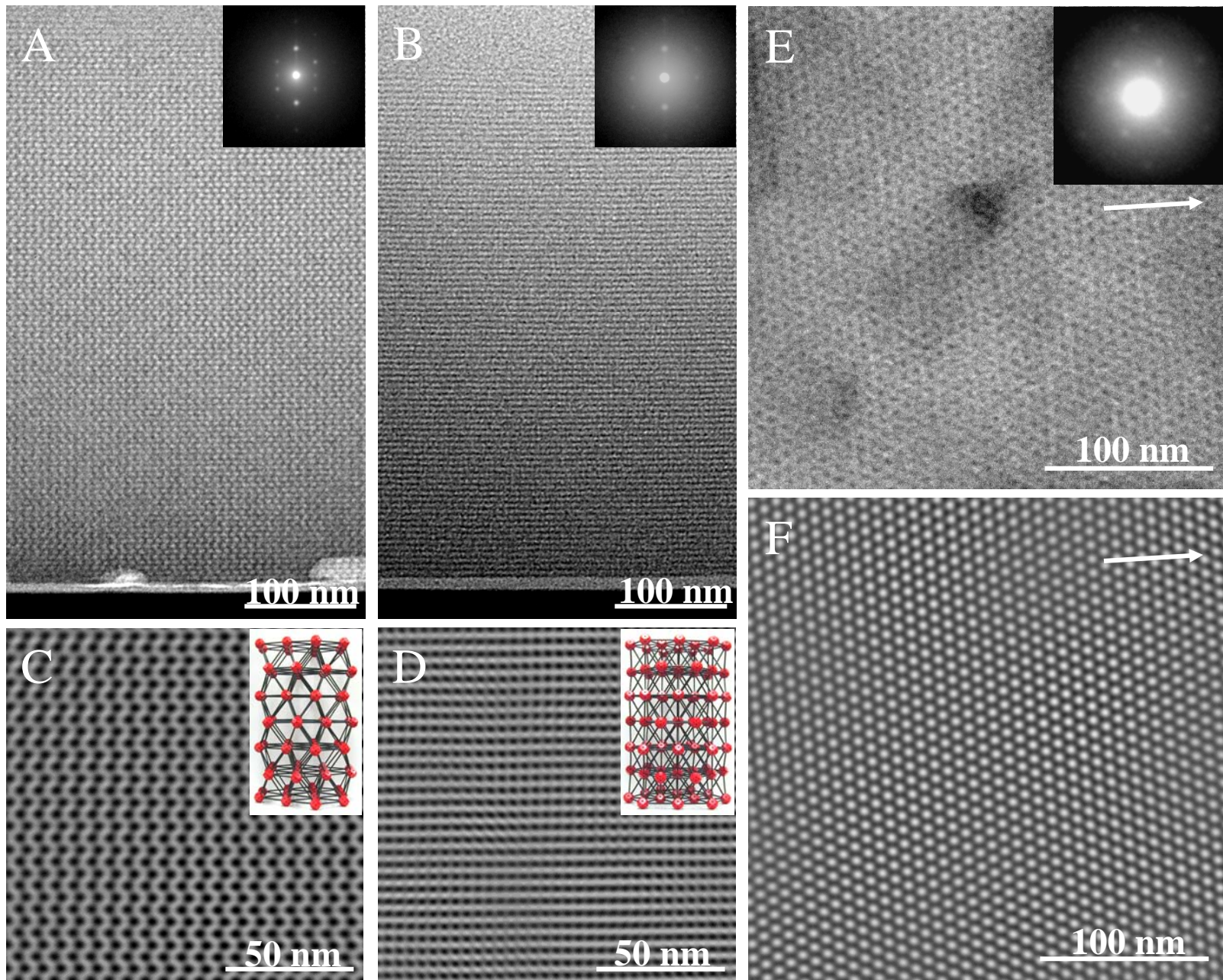


Requirements for the Polymer

1. Hydrophobicity
2. Susceptibility for Rubbing (Flexibility)
3. Linearity

Single crystalline porous structure of mesoporous silica films





Variation of the porous structure

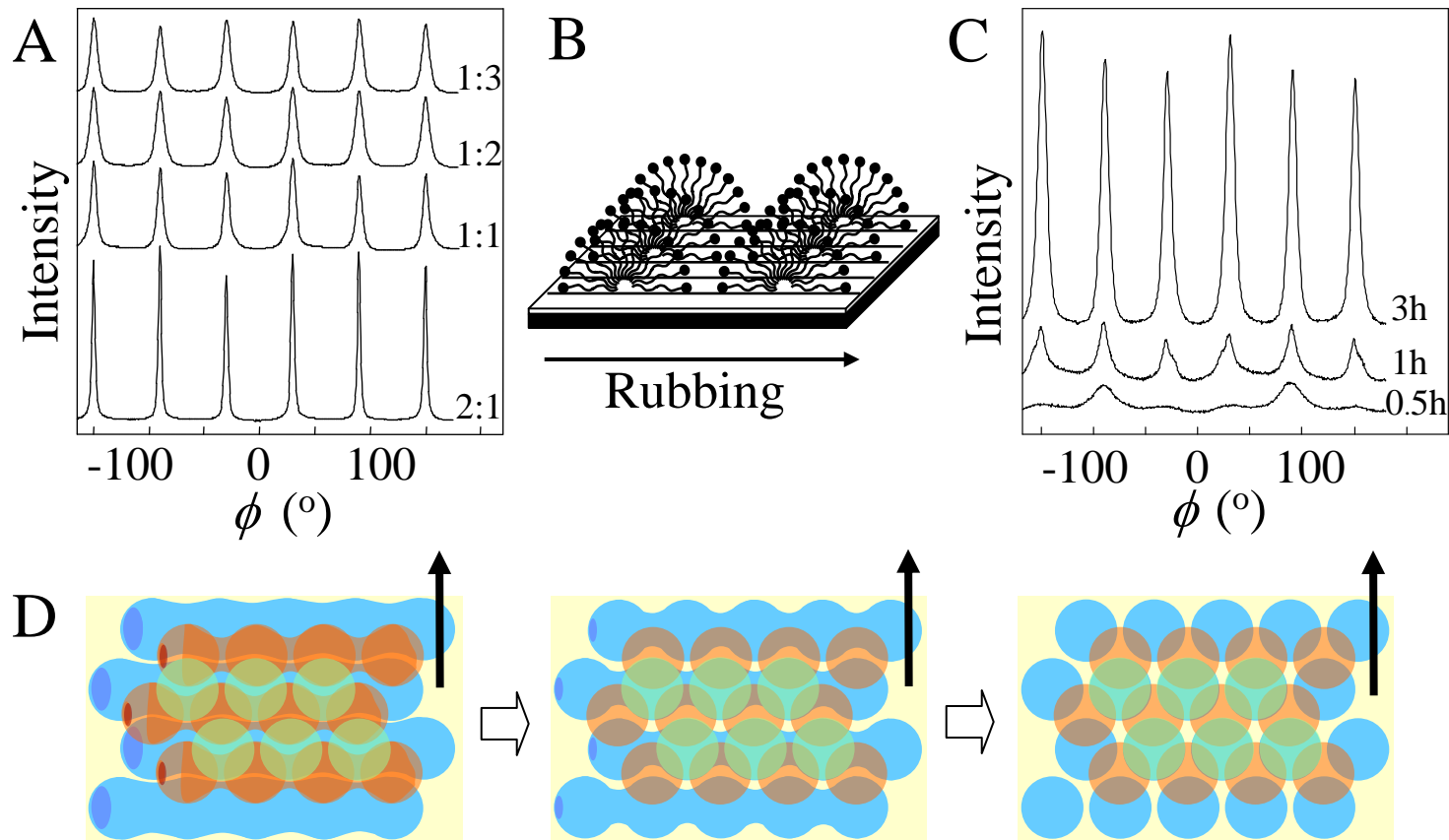
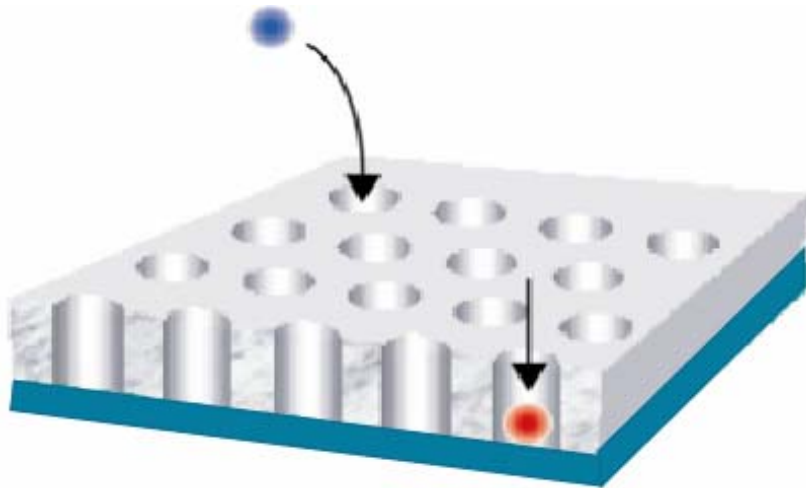


Figure 3

Perpendicular alignment of mesochannels

High accessibility
High permeability



Novel Applications

- High-sensitive chemical sensors
- Ultra-high-density recording media
- Highly selective separations

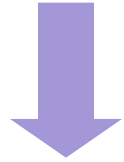
Uniform arrangement of guest species in nanometer order

Many approaches have been developed toward the perpendicular alignment.

- Electric field
- Ternary surfactants system
- Utilizing porous anodic alumina membrane
- Eutectic decomposition and chemical etching
- Microphase separation and control of interfacial energy

Mesophase Alignment in High Magnetic Field

Surfactant (diamagnetic substance)



Lyotropic Liquid Crystals (LLC)

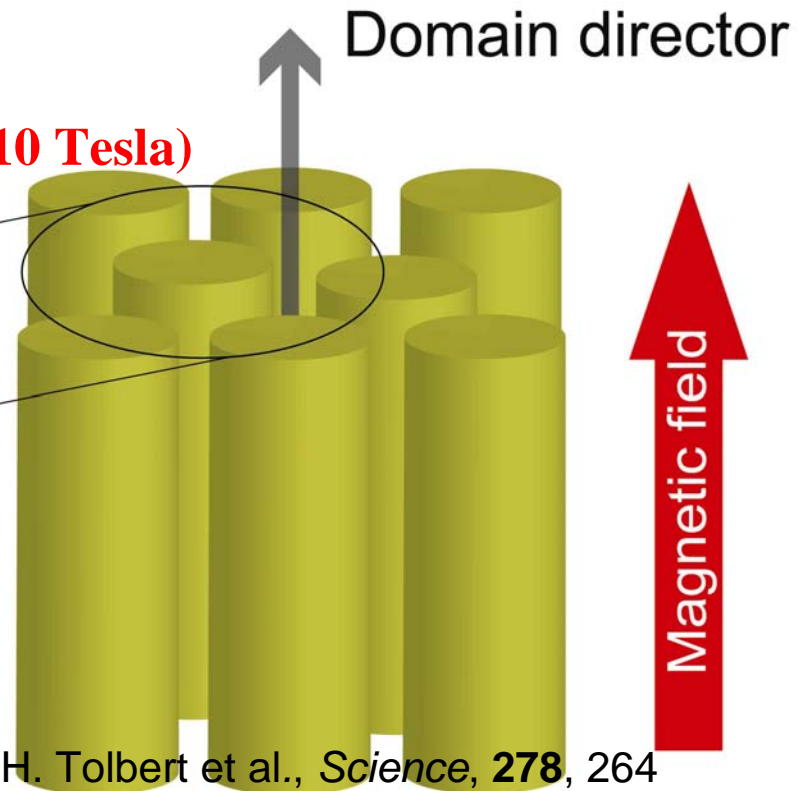
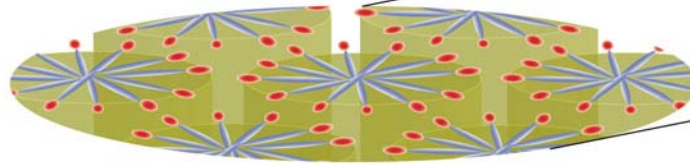


High magnetic field (higher than 10 Tesla)

Magnetic transition



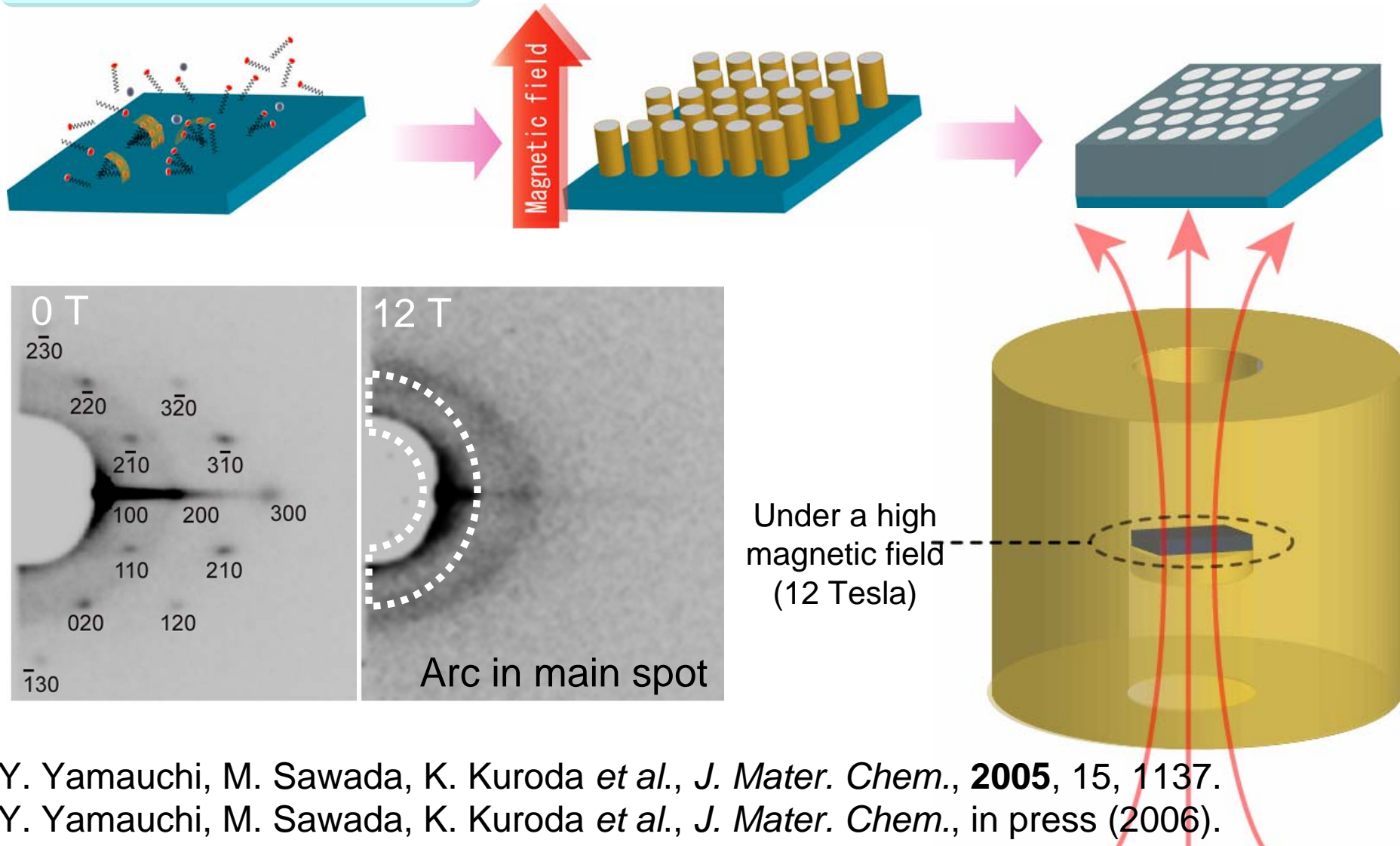
**Macroscopically Oriented
Mesophase**



A. Firouzi *et al.*, *J. Am. Chem. Soc.*, **119**, 9466 (1997); S. H. Tolbert *et al.*, *Science*, **278**, 264 (1997); T. Grigorova *et al.*, *Macromolecules*, **38**, 7430 (2005); A. Rapp *et al.*, *J. Phys. Chem. B*, **103**, 1705 (1999); M. Ogura *et al.*, 4th International Mesostructured Materials Symposium (IMMS), Book of abstracts p.386.

Magnetically induced orientation of mesochannels in mesoporous silica films

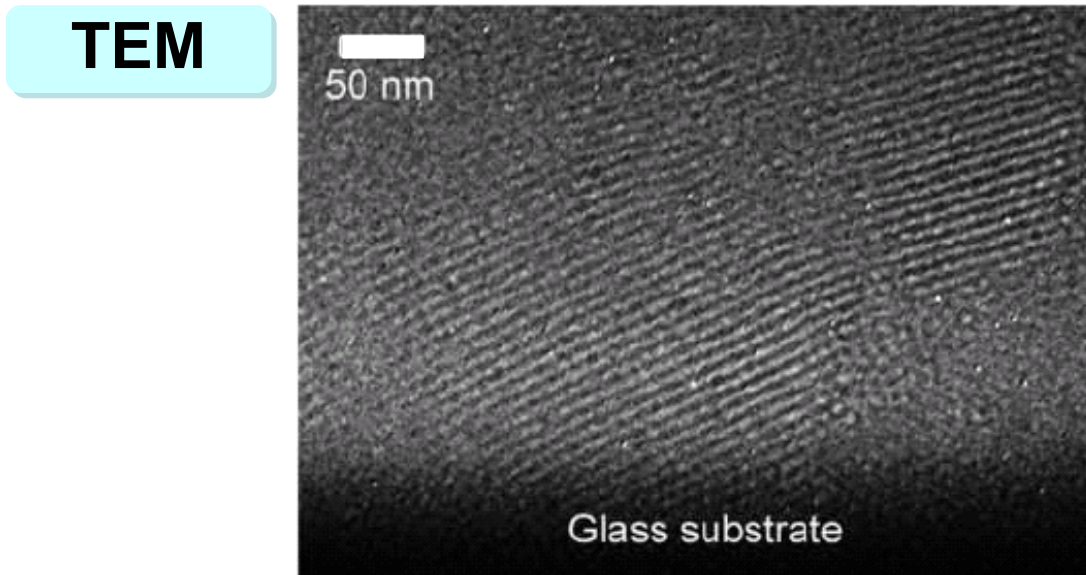
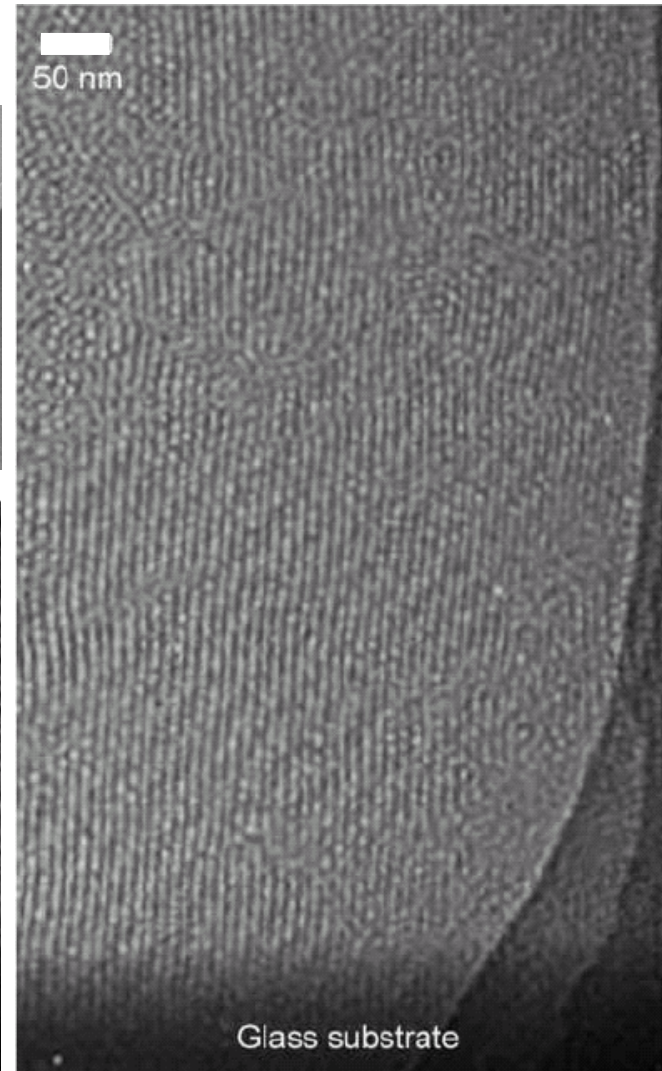
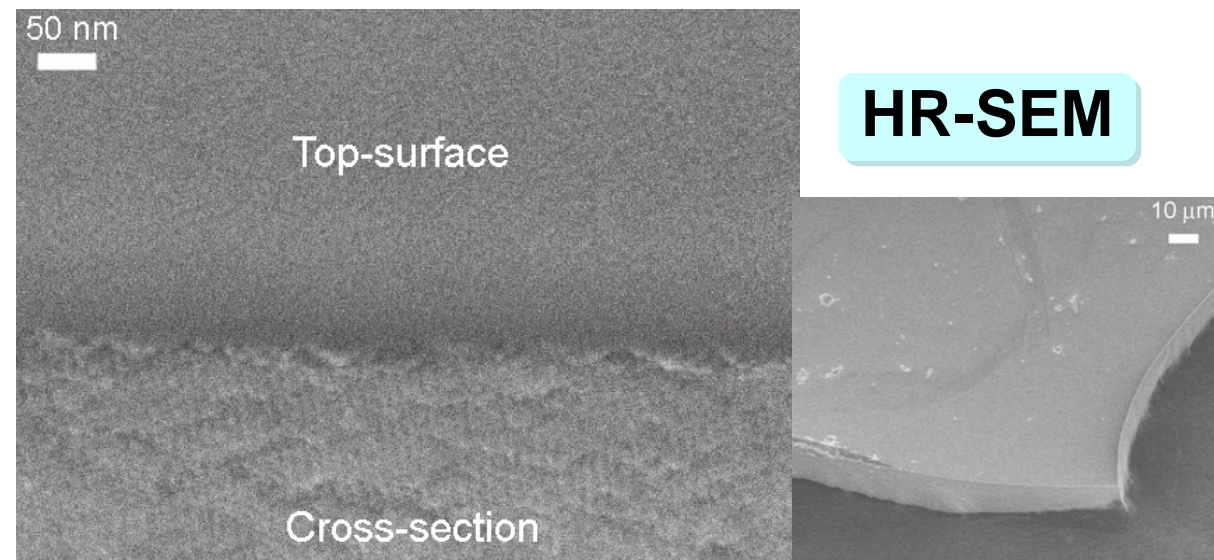
Formation Process



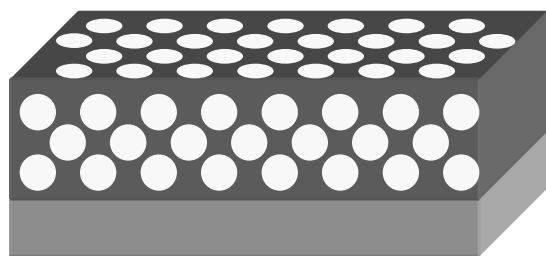
Y. Yamauchi, M. Sawada, K. Kuroda *et al.*, *J. Mater. Chem.*, **2005**, 15, 1137.

Y. Yamauchi, M. Sawada, K. Kuroda *et al.*, *J. Mater. Chem.*, in press (2006).

Magnetically induced Orientation

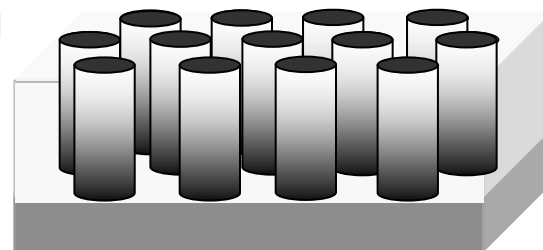


Synthesis of crystalline mesoporous TiO₂ thin films with a vertical porosity



3D hexagonal structure

Structural transformation



Nanopillar thin film with vertical porosity

- Appropriate reactant ratios
- Low aging temperatures

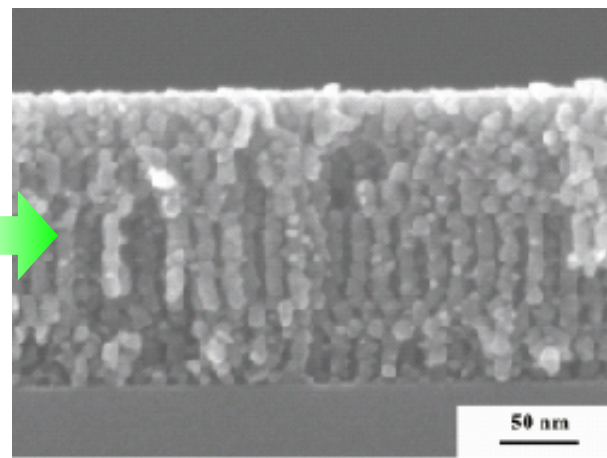
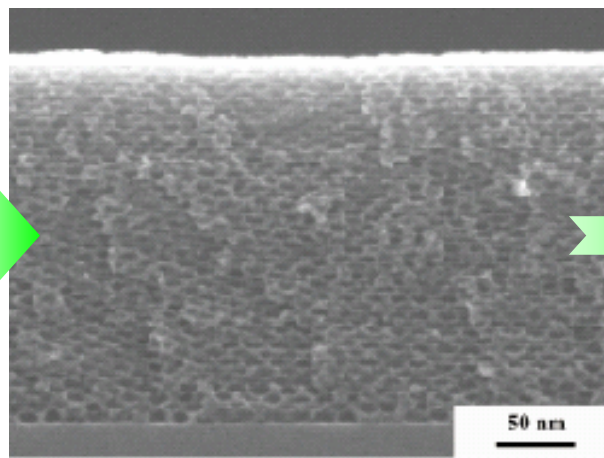
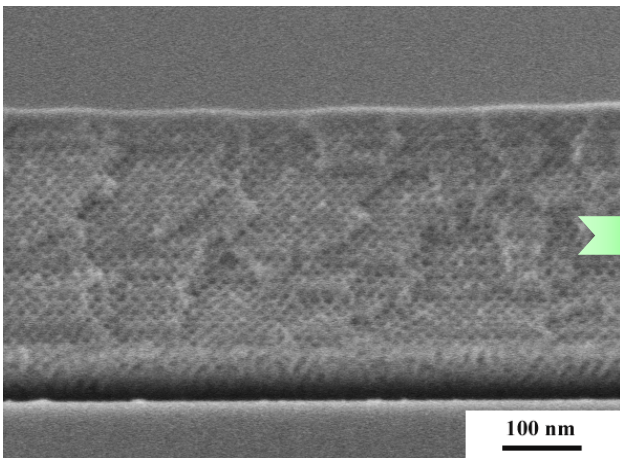
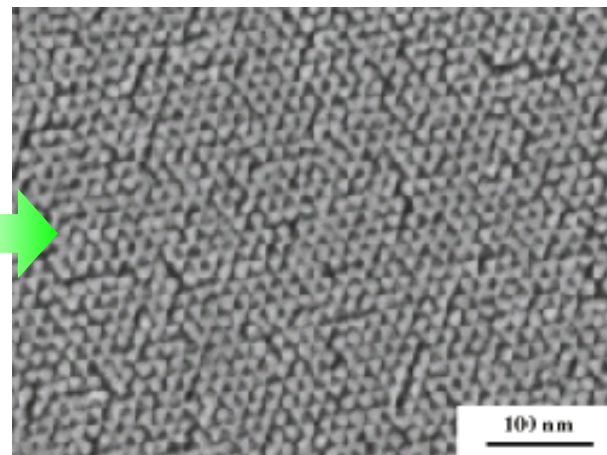
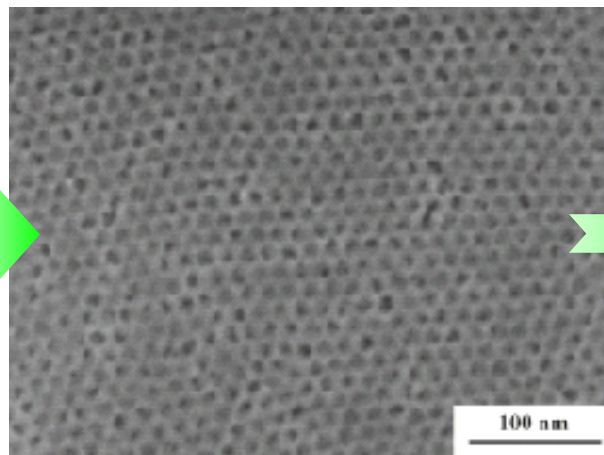
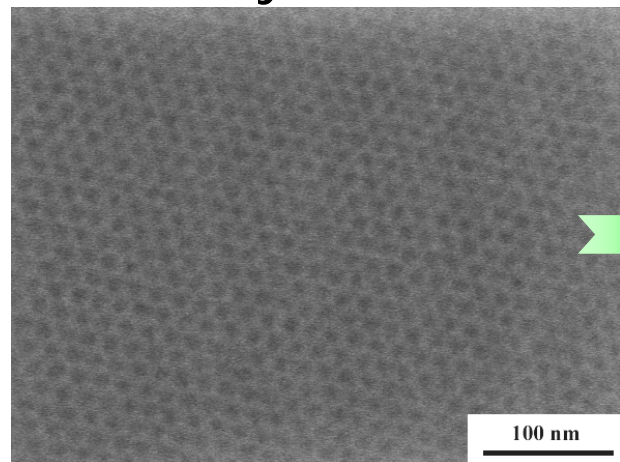
- Crystalline pillars
- A vertical and continuous porosity

Results: FE-SEM Observation

As-synthesized

200°C

400°C

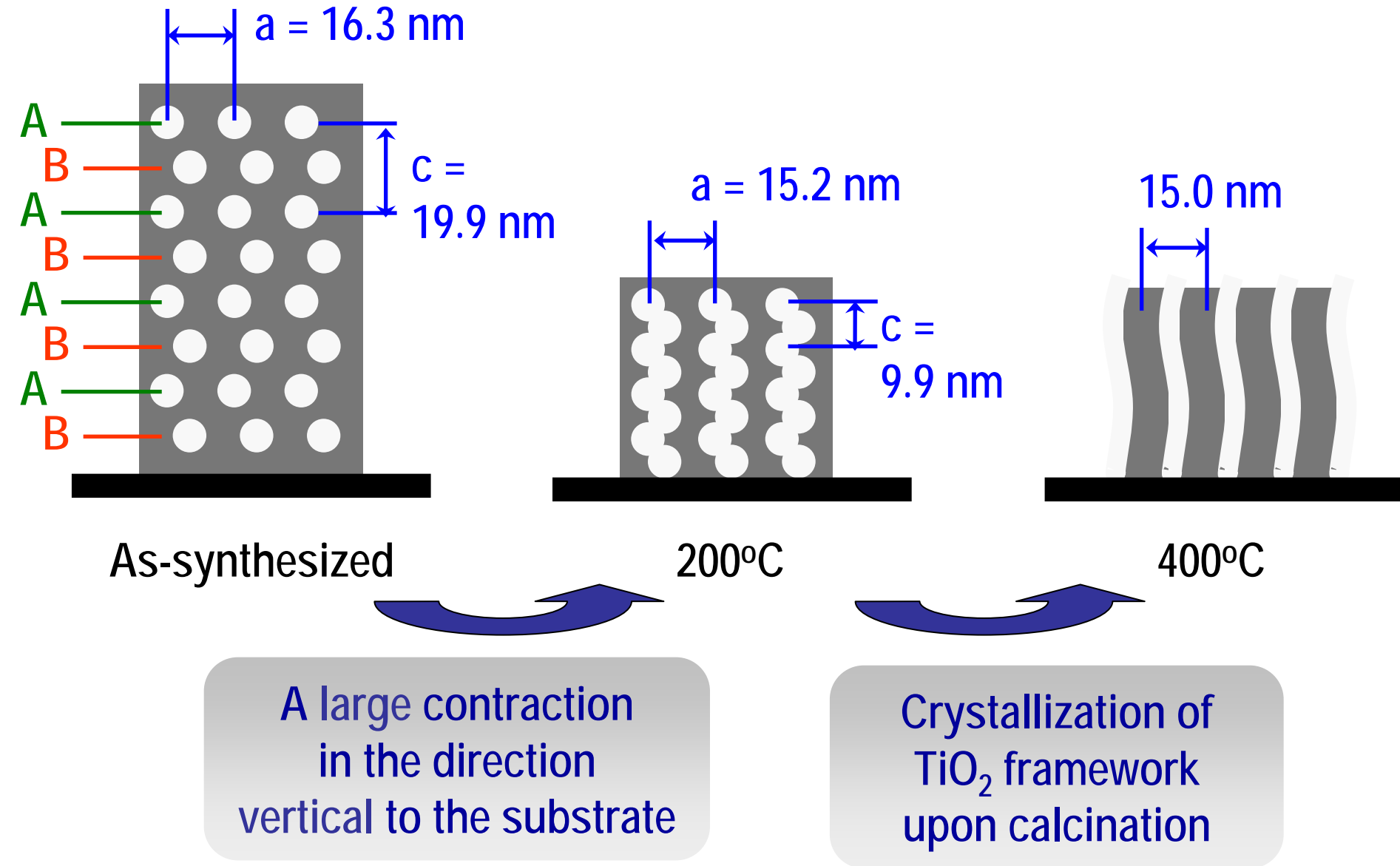


3D hexagonal
mesoporous structure

TiO₂ nanopillar arrays
with vertical porosity

Chia-Wen Wu et al., JACS (2006)

Discussion: Formation Mechanism of TiO₂ Pillars – Cross Section



Incorporation of Various Guest Species

Mesoporous Film

Guest Species

Combination

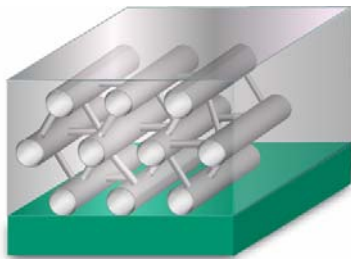
■ Control of Orientation, Conformation and Interactions

Guest Species

- Metal (Pt, Au, Ag, Ni...)
- Semiconductor (CdS, CdTe...)
- Carbon
- Dye (Cyanine, Rhodamine 6G, Spiropran...)
- Conductive Polymer (MEH-PPV...)

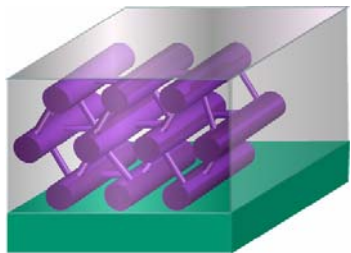
Well-aligned Pt Nanowires (1)

A: Mesoporous Silica Film



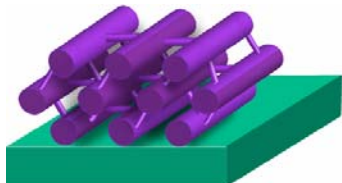
↓ Electrodeposition

B: Pt Nanowires / Silica

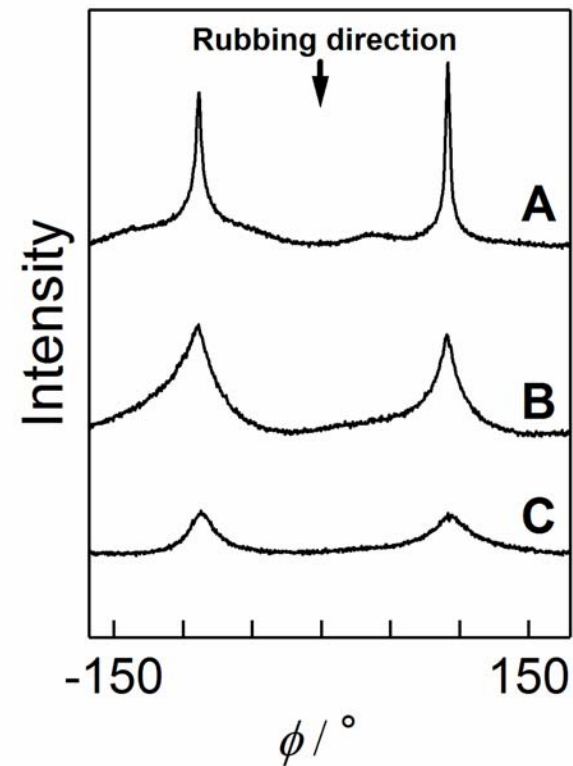


↓ Removal of Silica Template

C: Pt Nanowires Thin Film

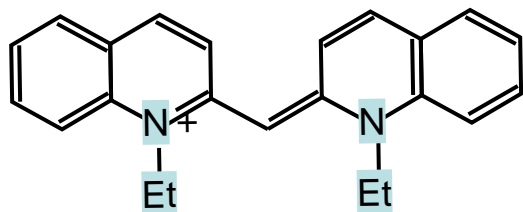


In-plane XRD



Incorporation of Dye (Cyanine Dye)

Cyanine Dye

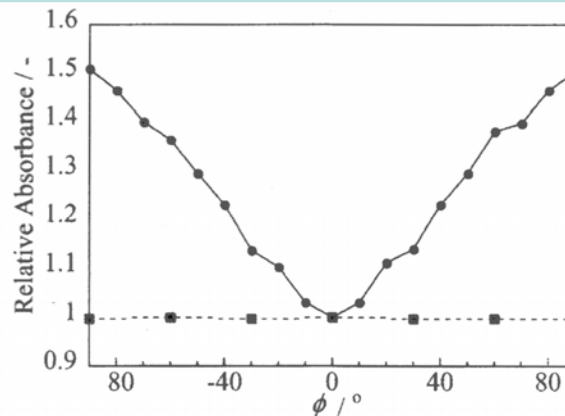


1.2 nm

+
Uniaxially Aligned
Mesoporous Structure

■ Alignment Control
of Cyanine Dye

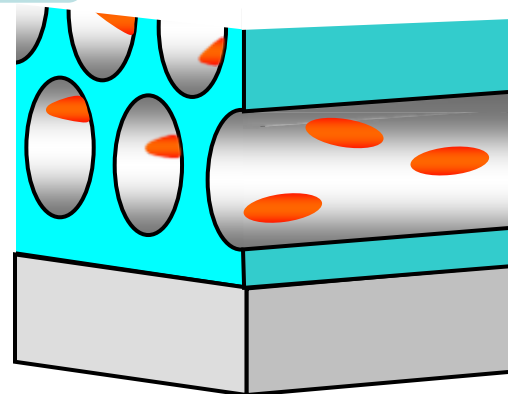
Polarization Dependence



● Well-Aligned Mesochannels

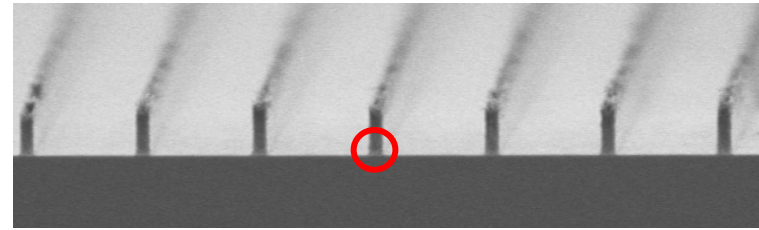
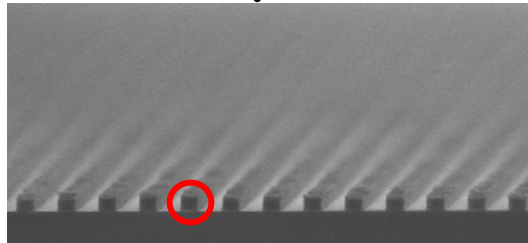
■ Random Alignment Mesochannels

Model

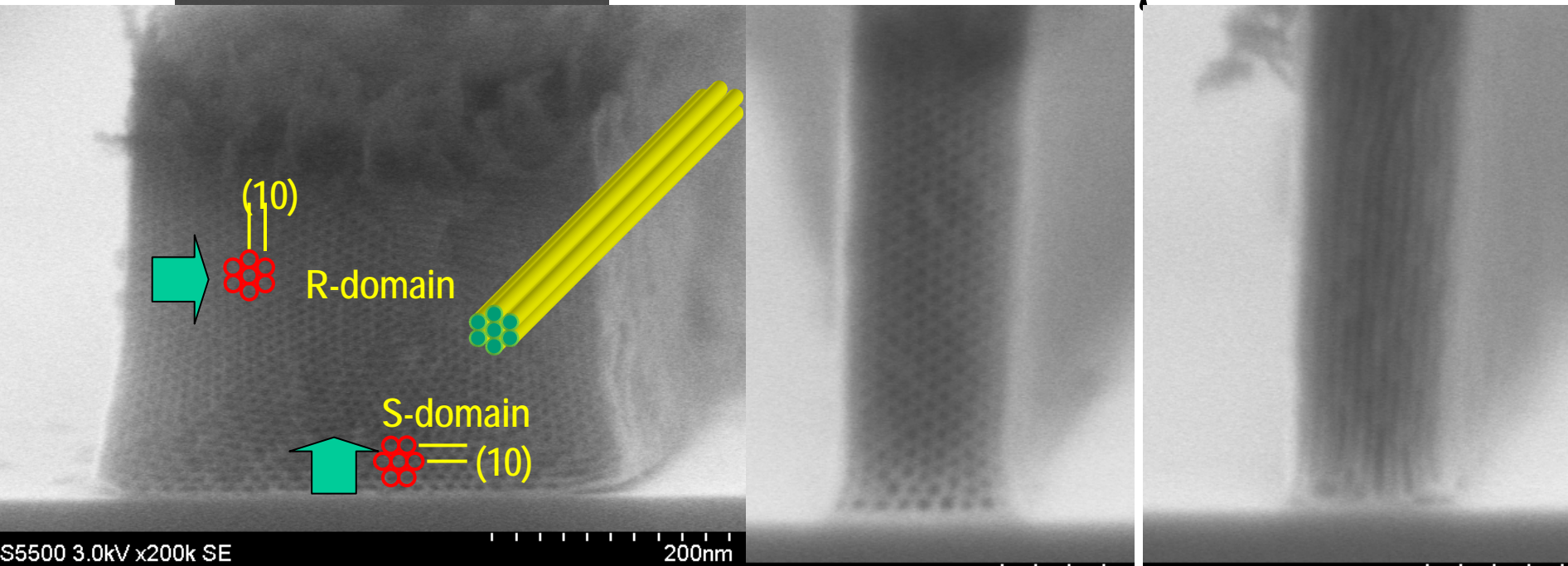


Orientation of mesochannels in line patterns

0.5- μm line

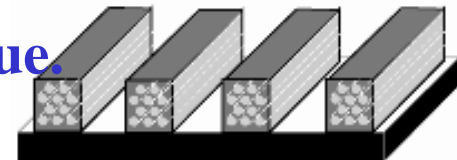


0.1- μm line



Filling the gap between lithography technique and molecular self-assembly.

Possibly exceeding the limitation of lithography technique.



OUTLINE

Background

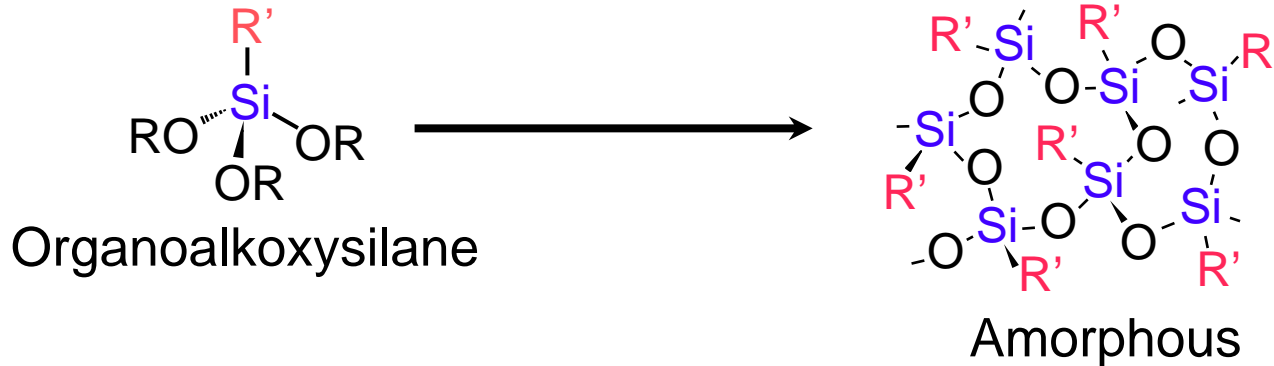
Mesoporous materials

Mesoporous films utilizing alkoxysilanes

Design of alkoxysilanes and self-assembly

Varieties and possibilities

Structural Control of Silica-Based Hybrid Materials



Motivation (from 1997)

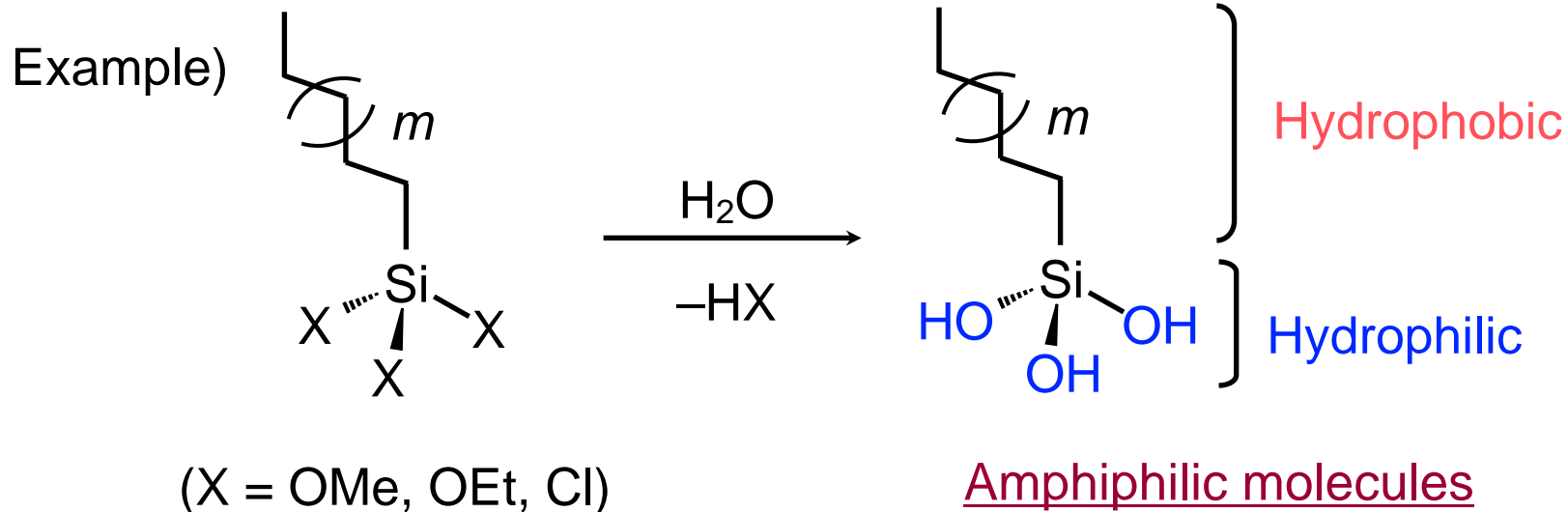
Nanostructural control of hybrids from organoalkoxysilanes
without the use of surfactant assemblies



Novel hybrid materials with unique nanostructures and properties

- Ordered arrangement of organic groups
- Structural control of siloxane framework

Design of amphiphilic molecules

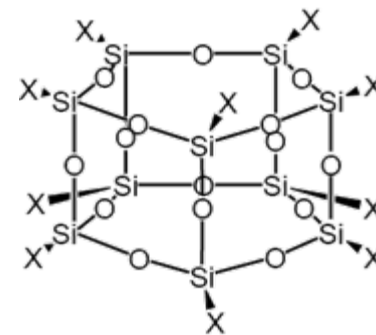
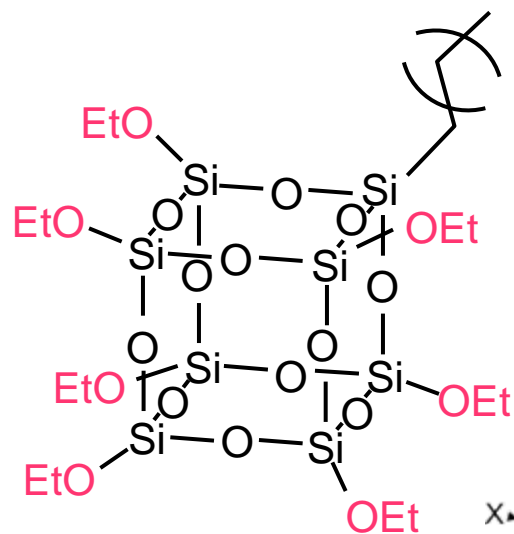
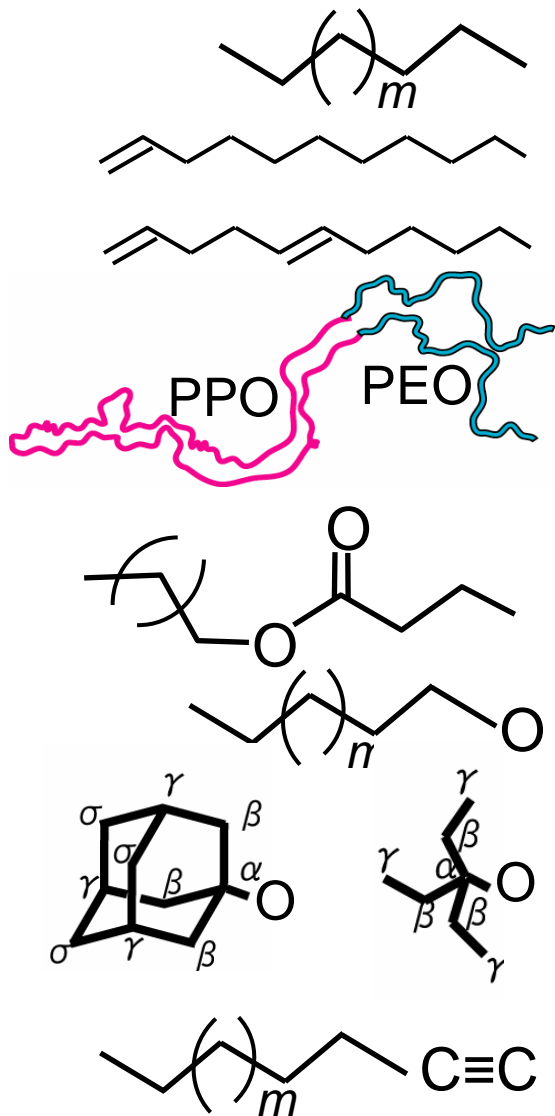


Self-Assembled Monolayers (SAMs) = 2D self-organization

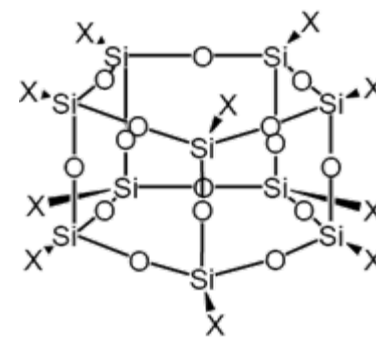
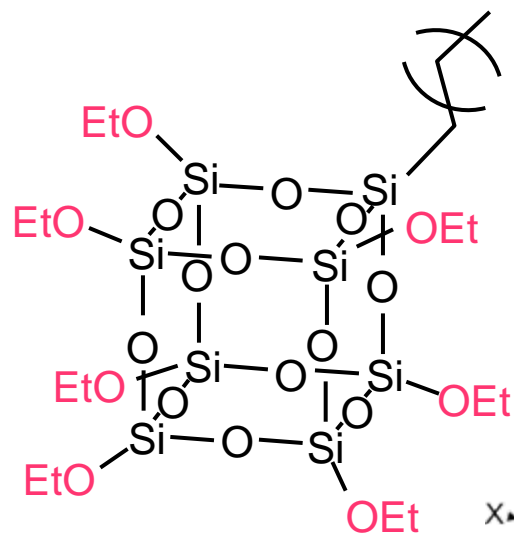
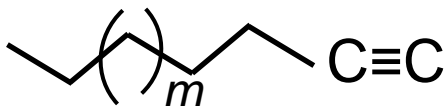
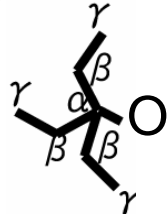
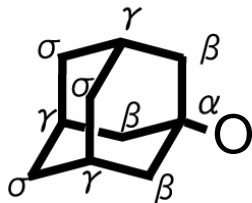
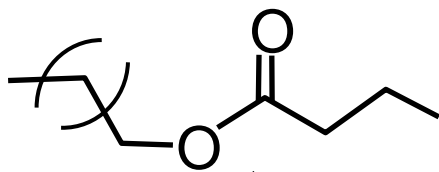
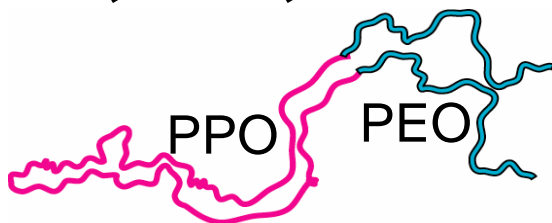
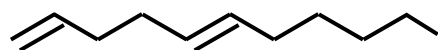
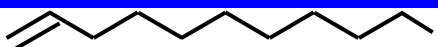
A. Ulman, *Chem. Rev.*, **96**, 1533 (1996).

Various assembled structures are expected to form by molecular design and control of reaction conditions

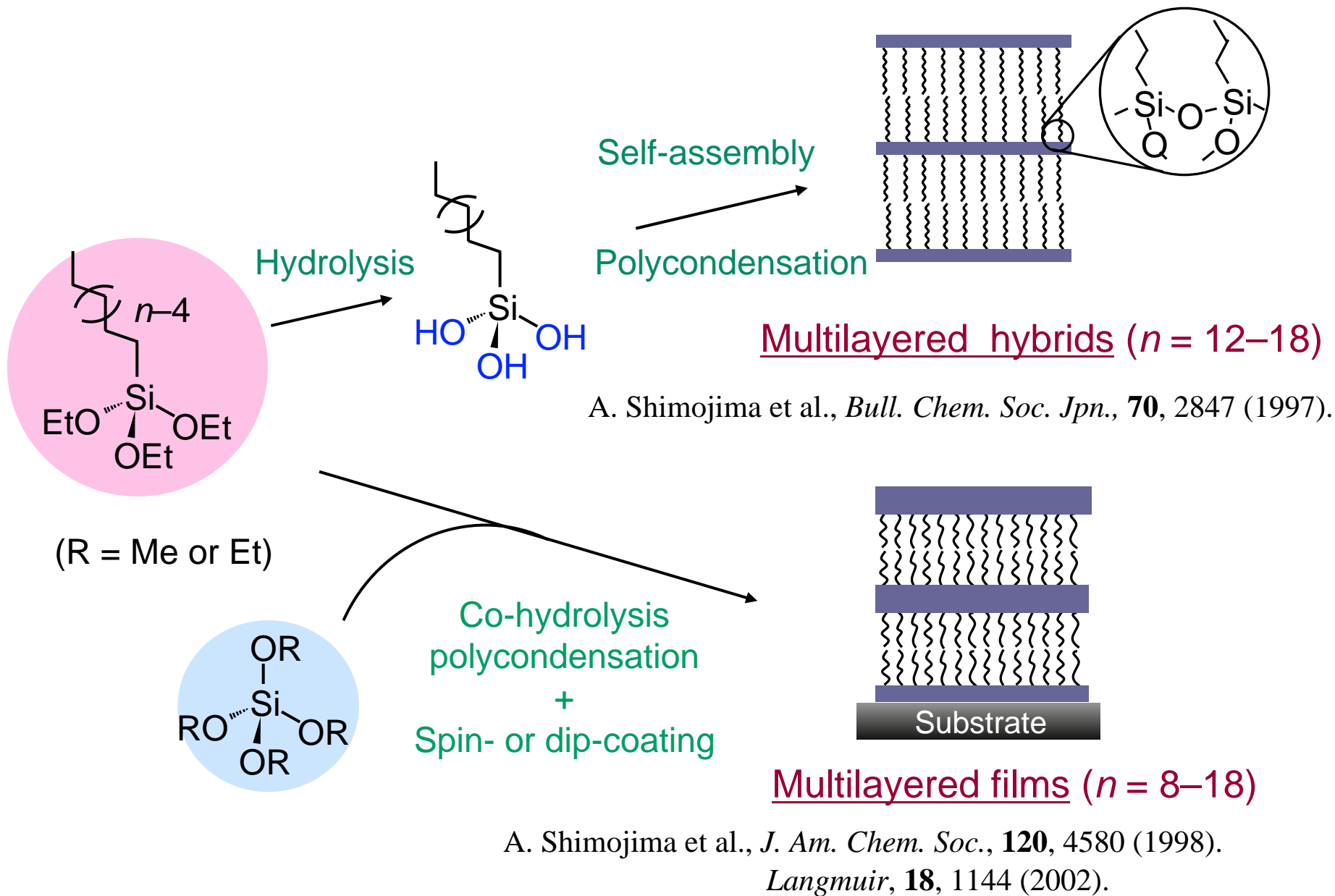
Varieties in organosilanes



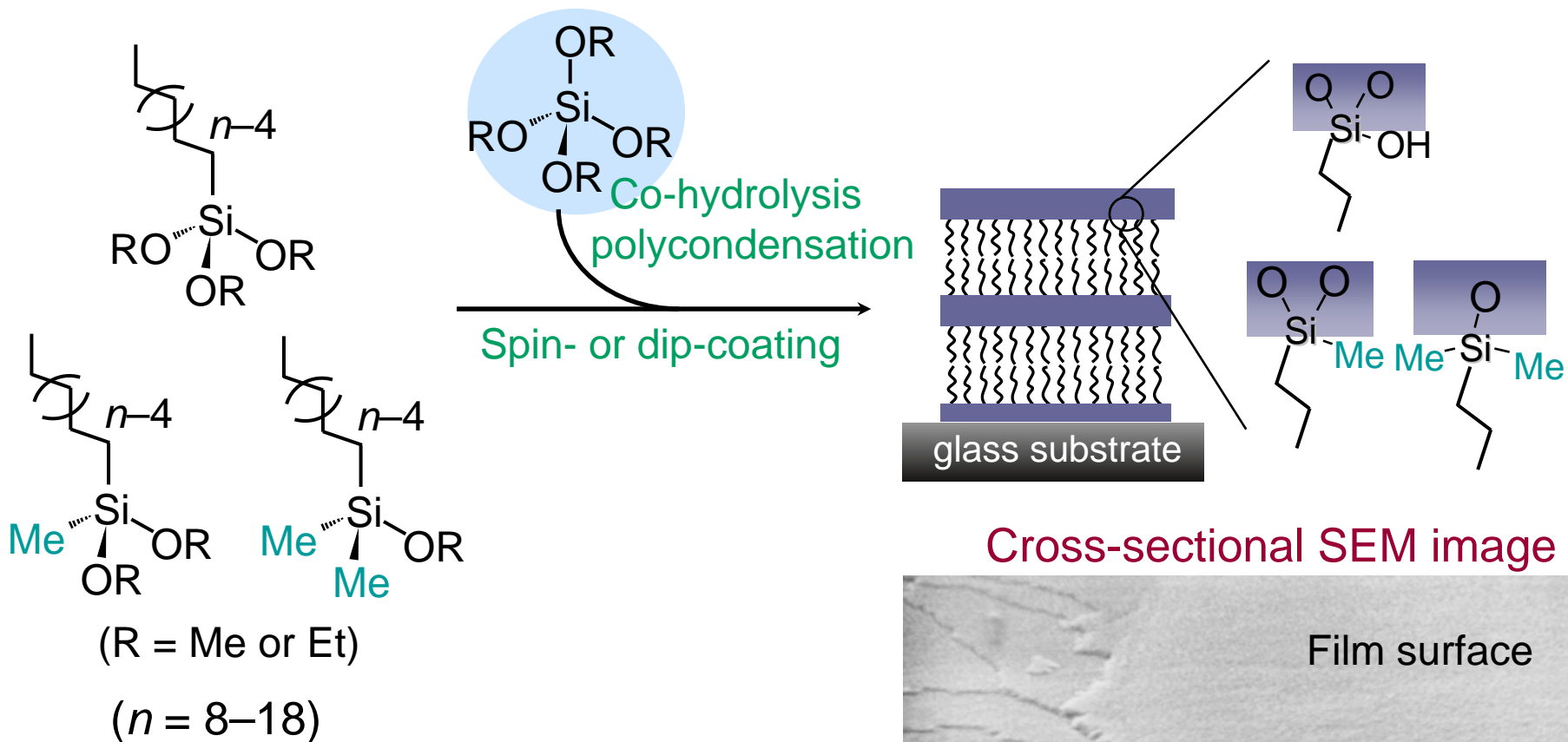
Varieties in organosilanes



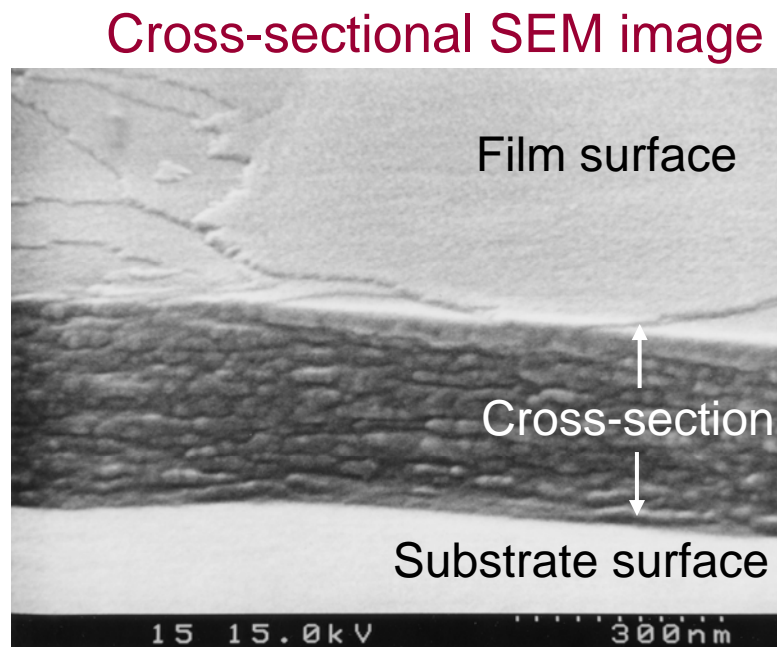
Our previous works



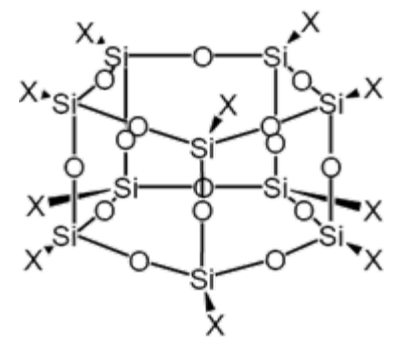
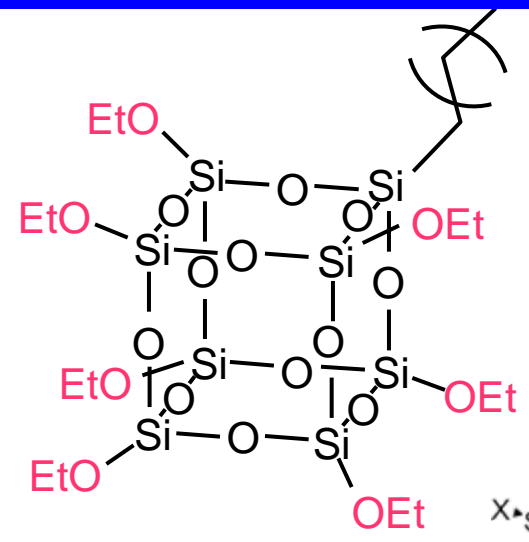
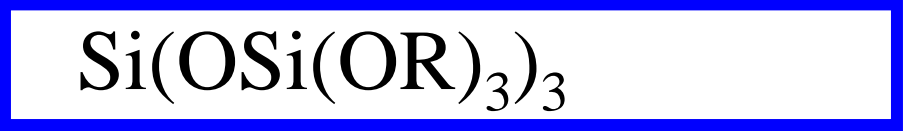
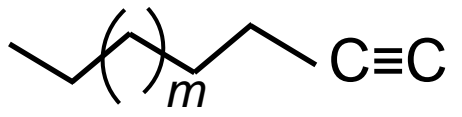
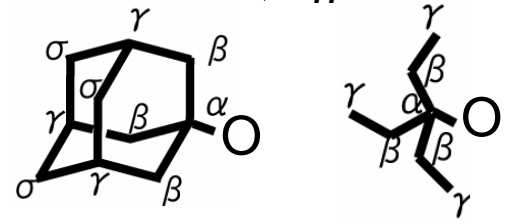
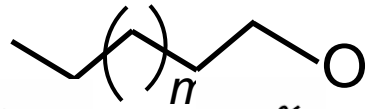
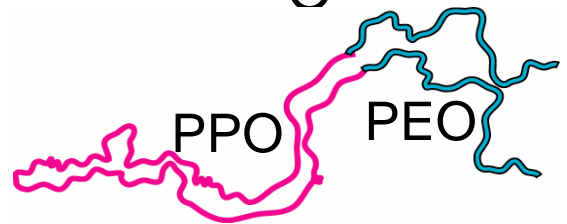
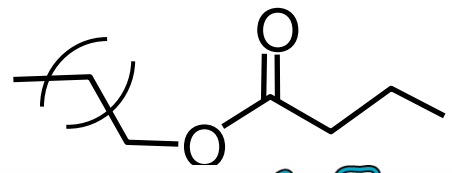
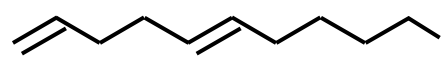
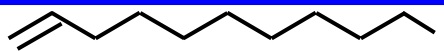
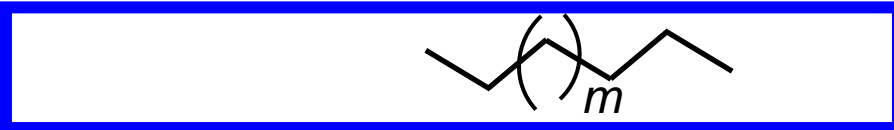
Formation of Layered Hybrid Films



A. Shimojima et al., *J. Am. Chem. Soc.*, **120**, 4580 (1998), *Chem. Mater.*, **13**, 3610 (2001), *Langmuir*, **18**, 1144 (2002).

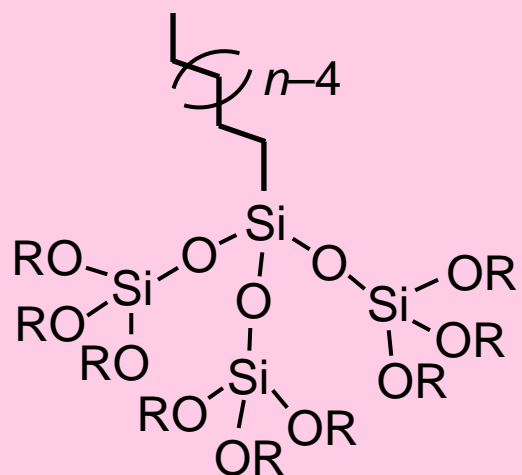


Varieties in organosilanes



Molecular Design of Oligosiloxane Precursors

Novel siloxane oligomers with alkyl chains
= single precursors



R = Me

$1(C_n)$ ($n = 4-18$)

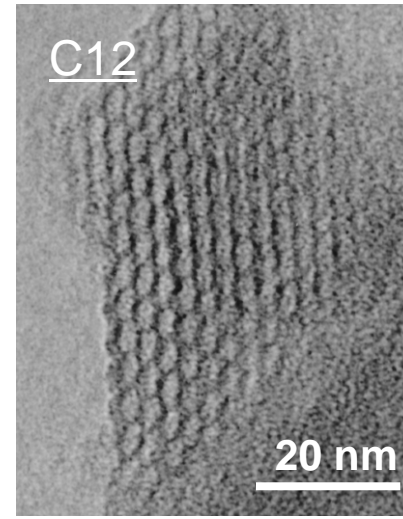
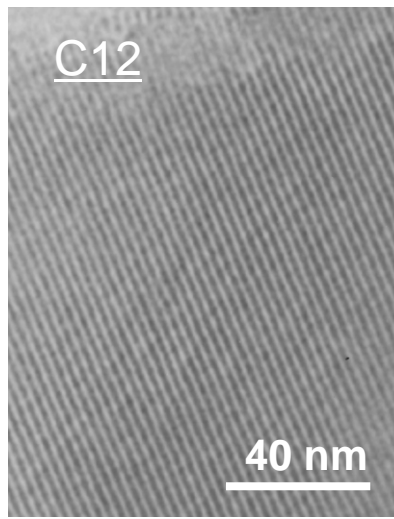
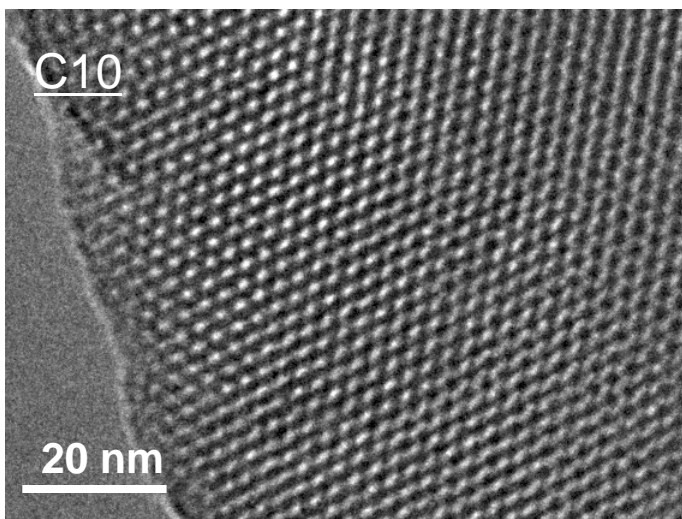
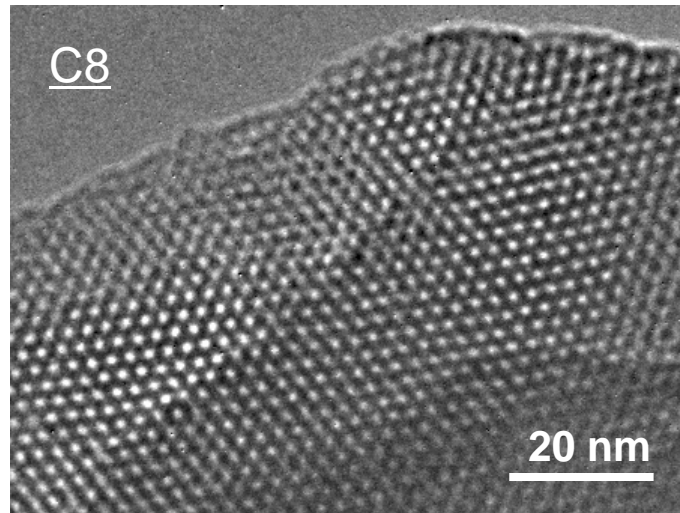
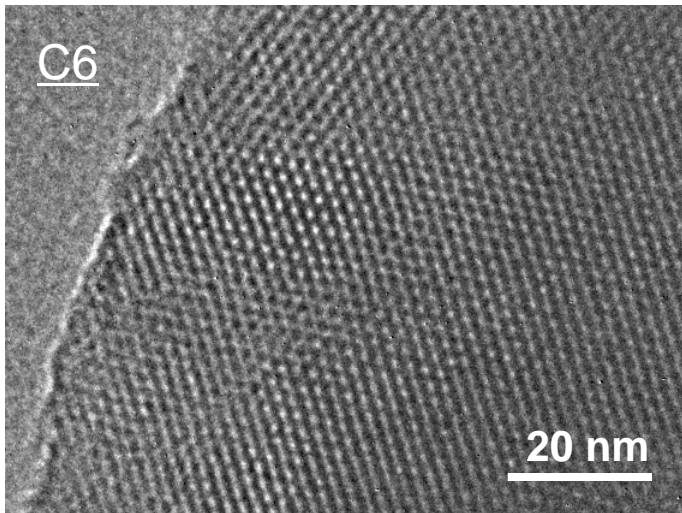
{ Well-defined molecular shape
Self-assembling ability
High network-forming ability



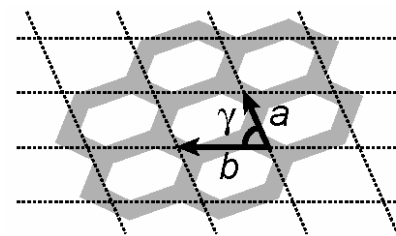
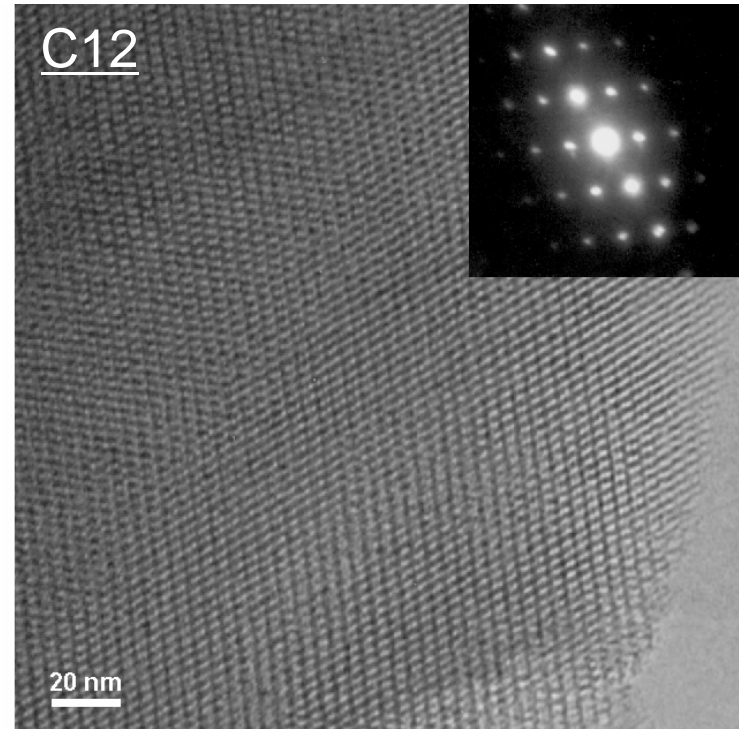
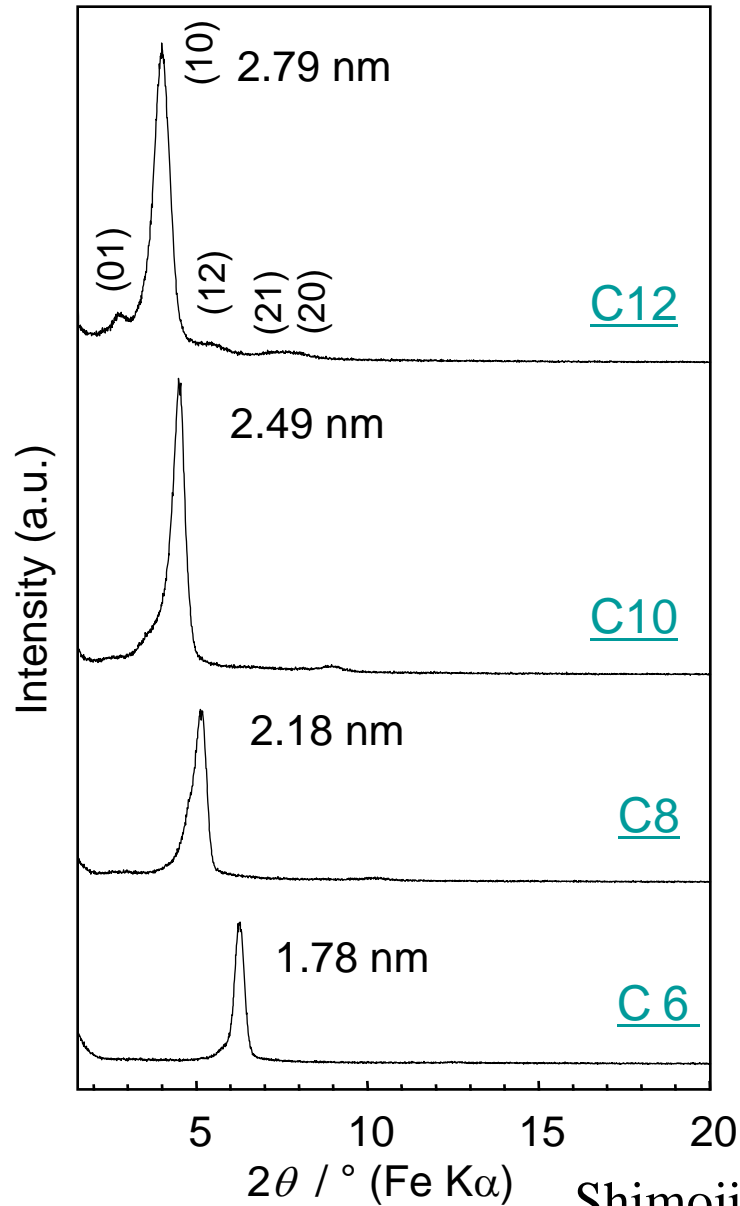
Better control of

- Reaction process
- Nanostructure & morphology of the products

TEM Images (as-made samples)

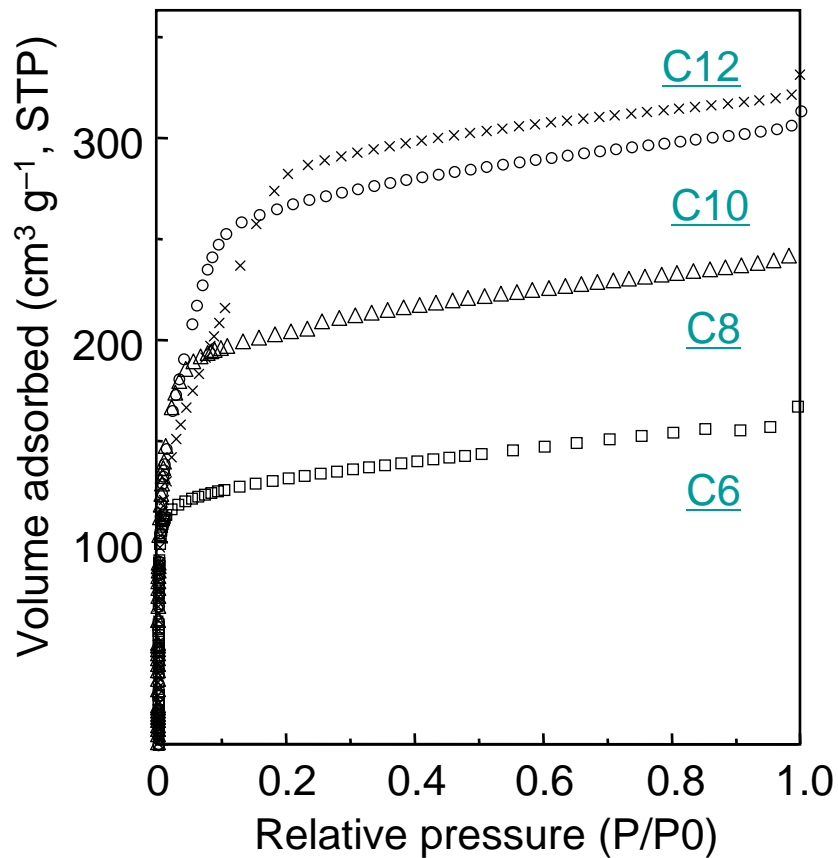


XRD Patterns (calcined samples)



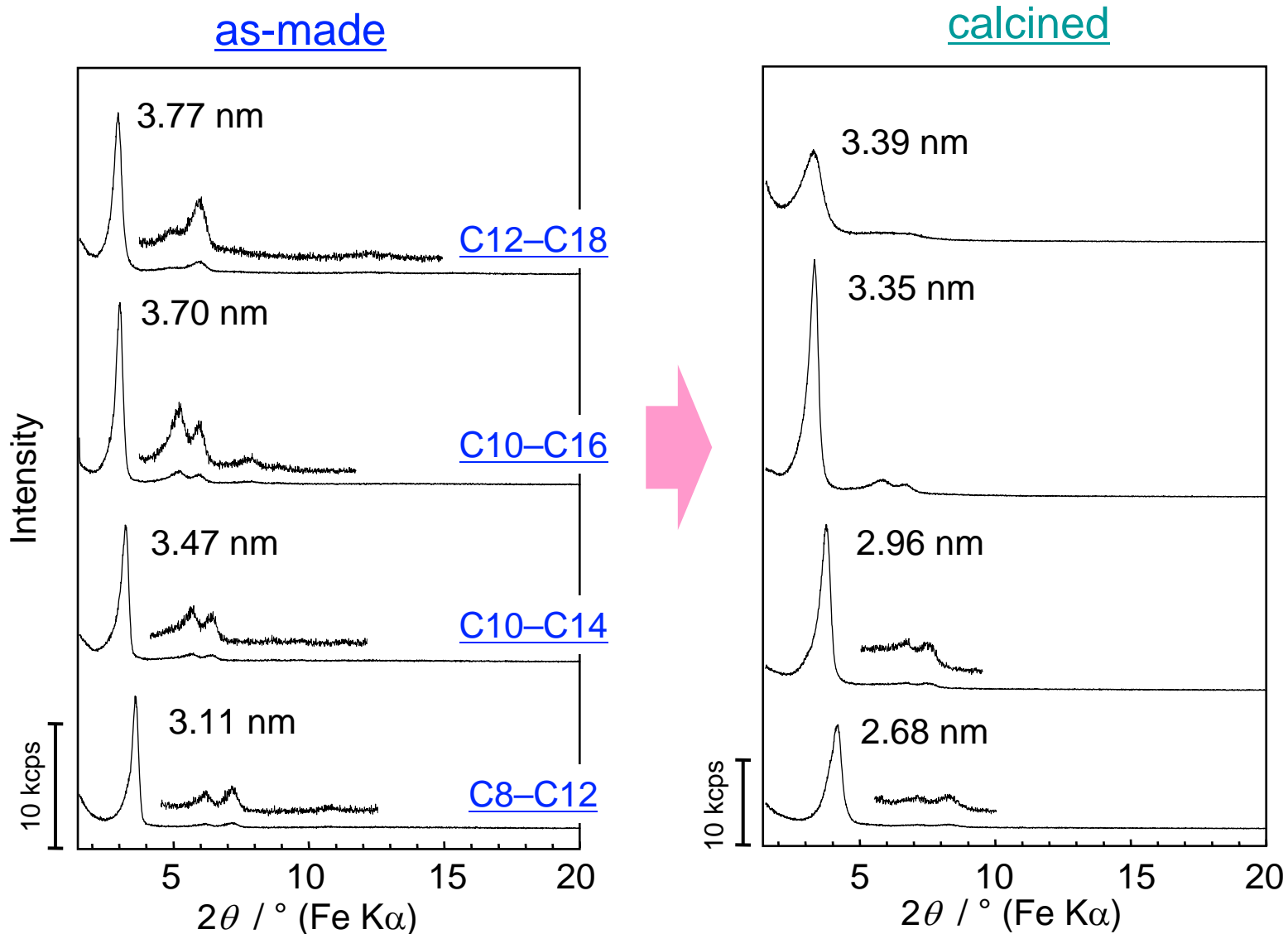
2D monoclinic structure

N₂ adsorption isotherms (calcined samples)

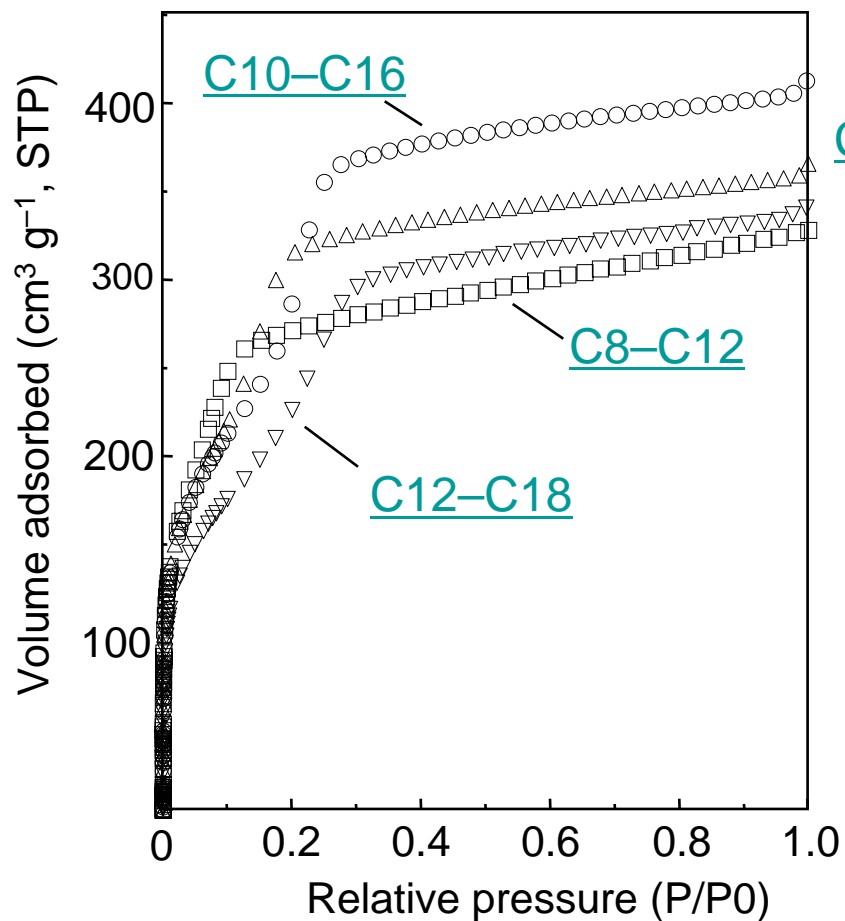


<i>n</i>	BET surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	NLDFT pore diameter (nm)
C6	510	0.22	1.1
C8	840	0.34	1.7
C10	950	0.43	2.2
C12	800	0.46	2.7

XRD Patterns - Binary systems of 1(Cn) with different chain lengths -

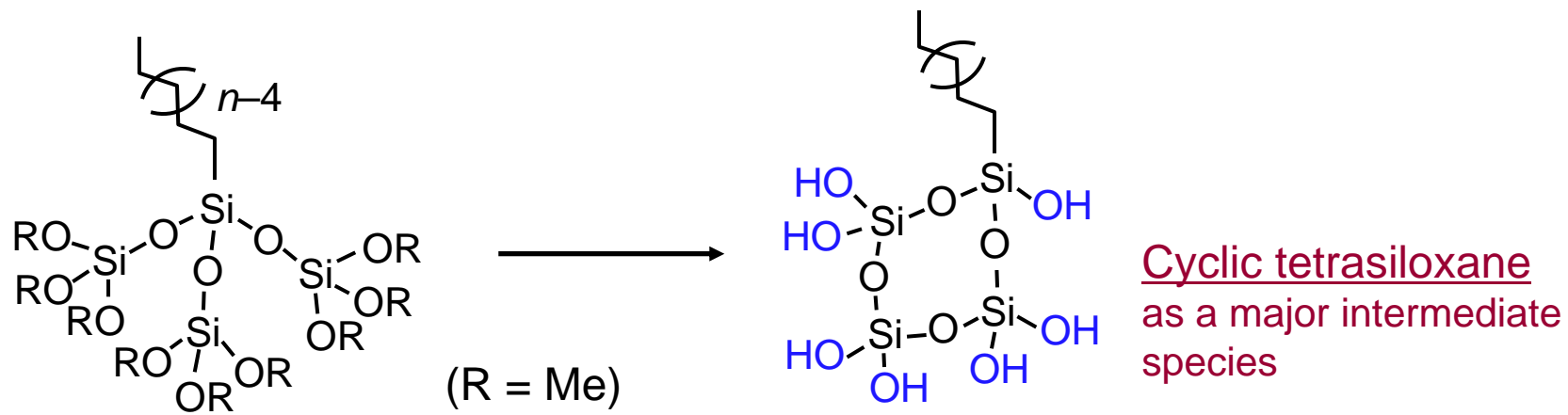


N₂ adsorption isotherms (calcined samples)



<i>n</i>	BET surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	NLDFT pore diameter (nm)
C8-C12	880	0.46	2.3
C10-C14	840	0.51	2.8
C10-C16	830	0.58	3.2
C12-C18	690	0.49	3.3

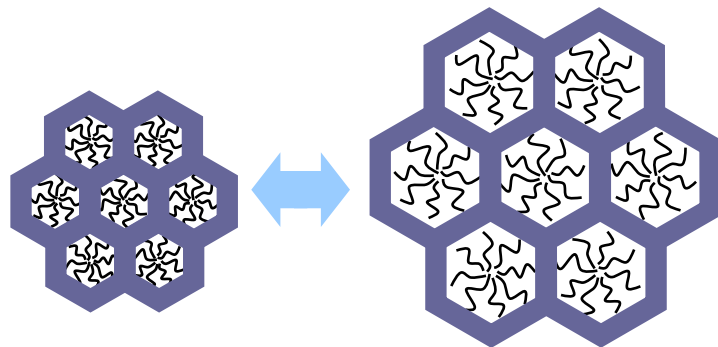
Self-assembly processes of 1(Cn)



Cyclic tetrasiloxane
as a major intermediate
species

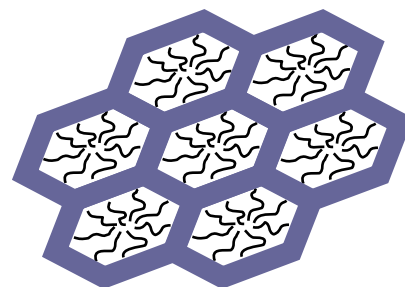
= Single precursors

Self-assembly



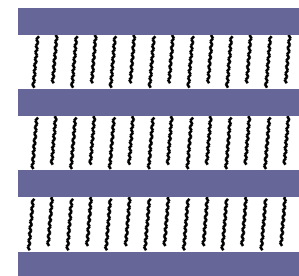
($n = 6-10, n = 10+16$ etc.)

2D Hexagonal



($n = 12$)

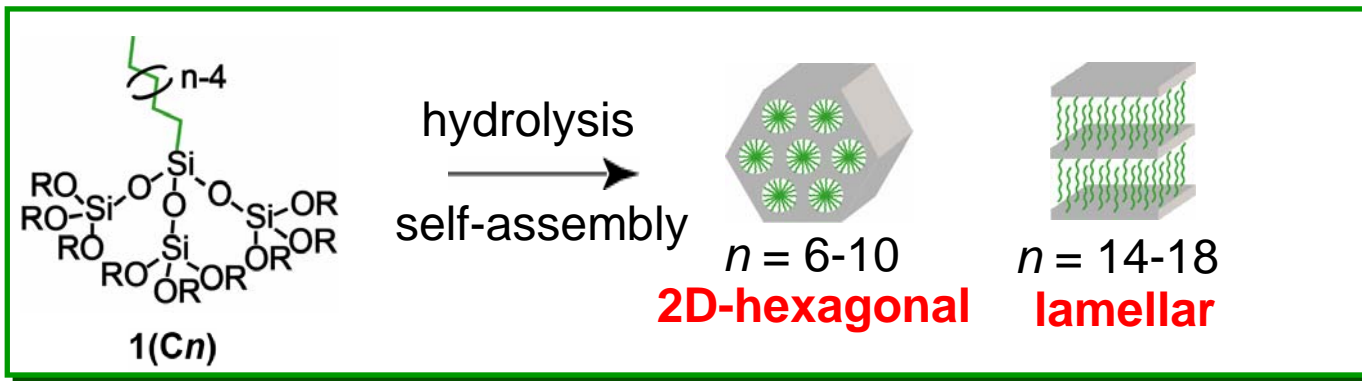
2D Monoclinic



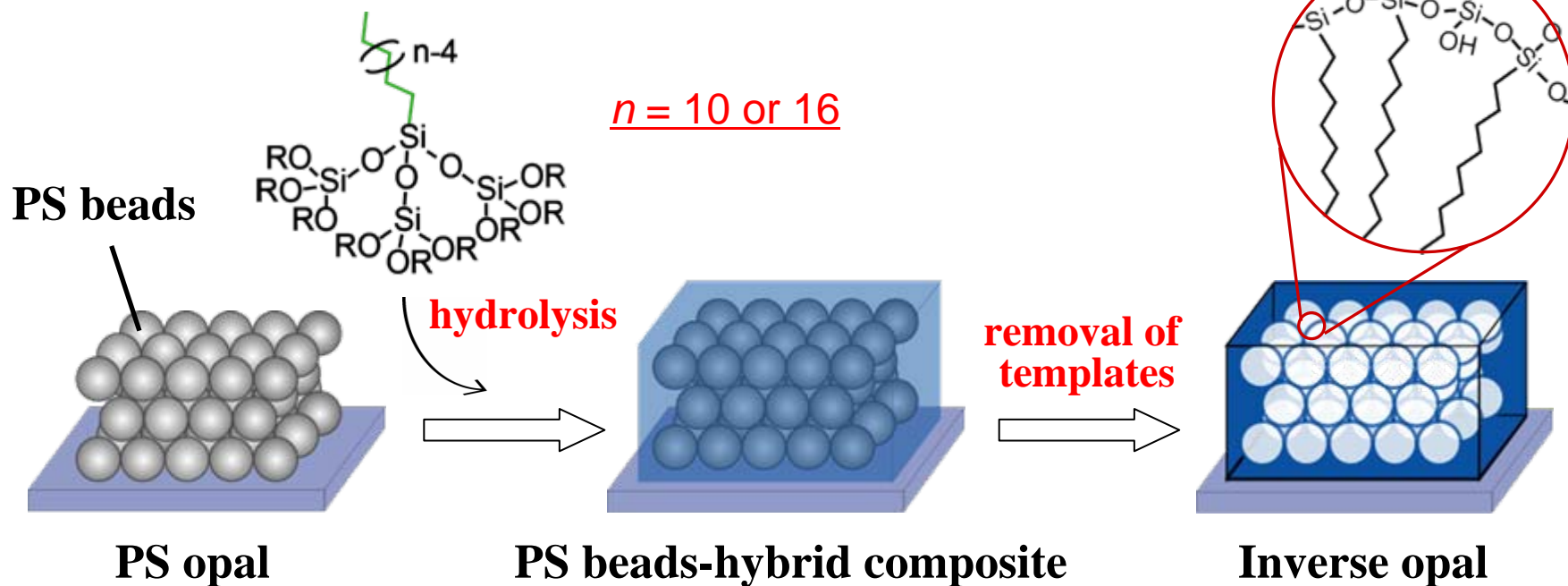
($n = 14-18$)

Lamellar

Mesostructured Siloxane-Organic Hybrid Films with Ordered Macropores



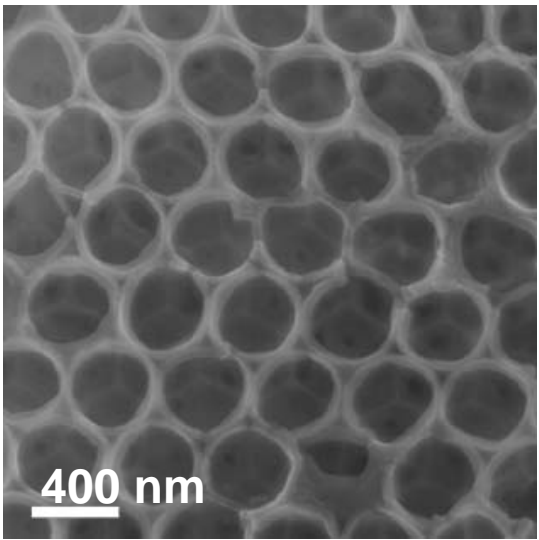
A. Shimojima, et al., *J. Am. Chem. Soc.*, **127**, 14108 (2005).



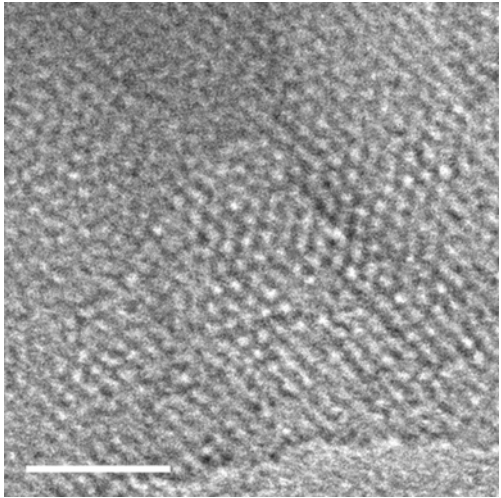
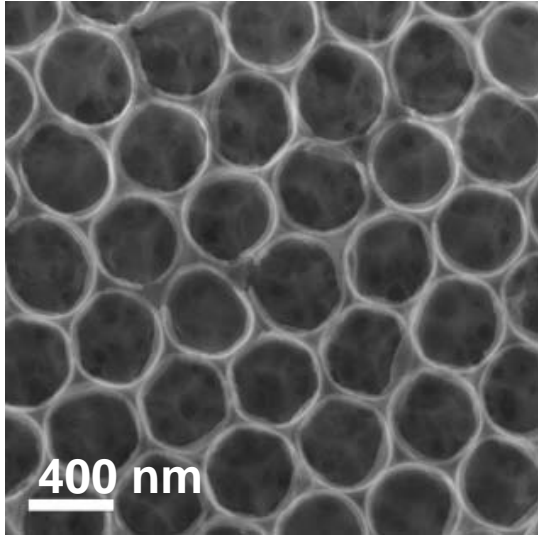
M. Sakurai, A. Shimojima, K. Kuroda, *Langmuir*, in press (2007).

Inverse opal film

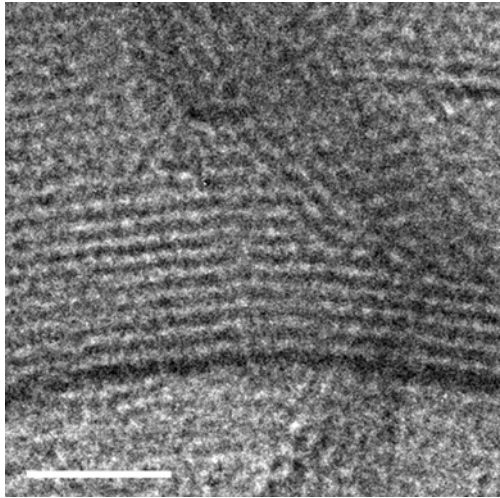
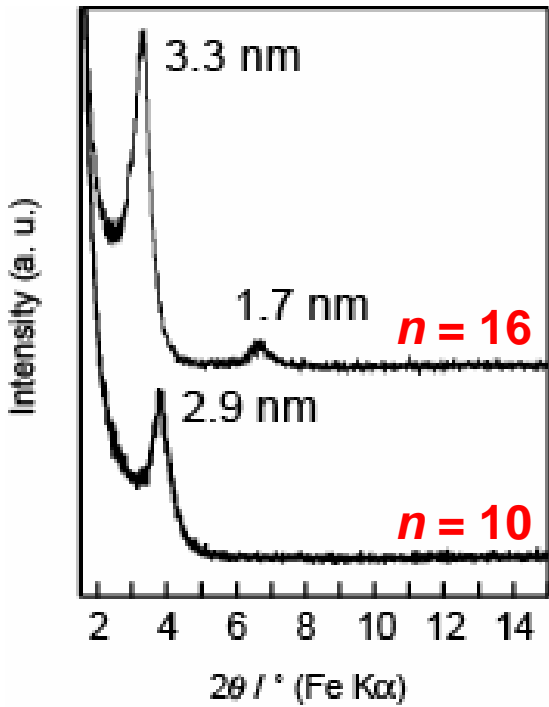
⟨ $n = 10$ ⟩



⟨ $n = 16$ ⟩

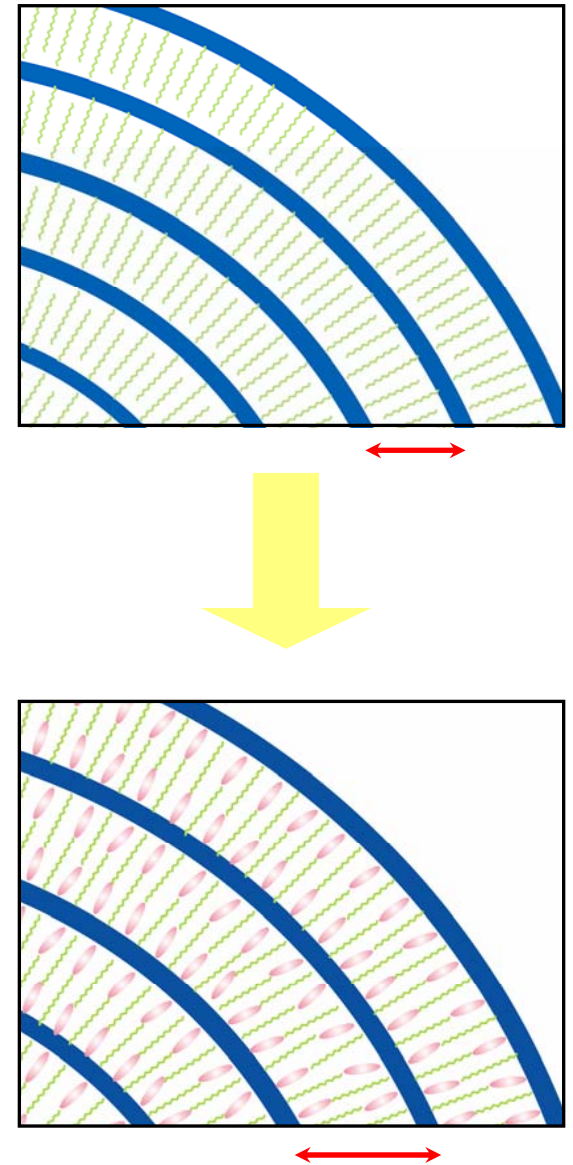
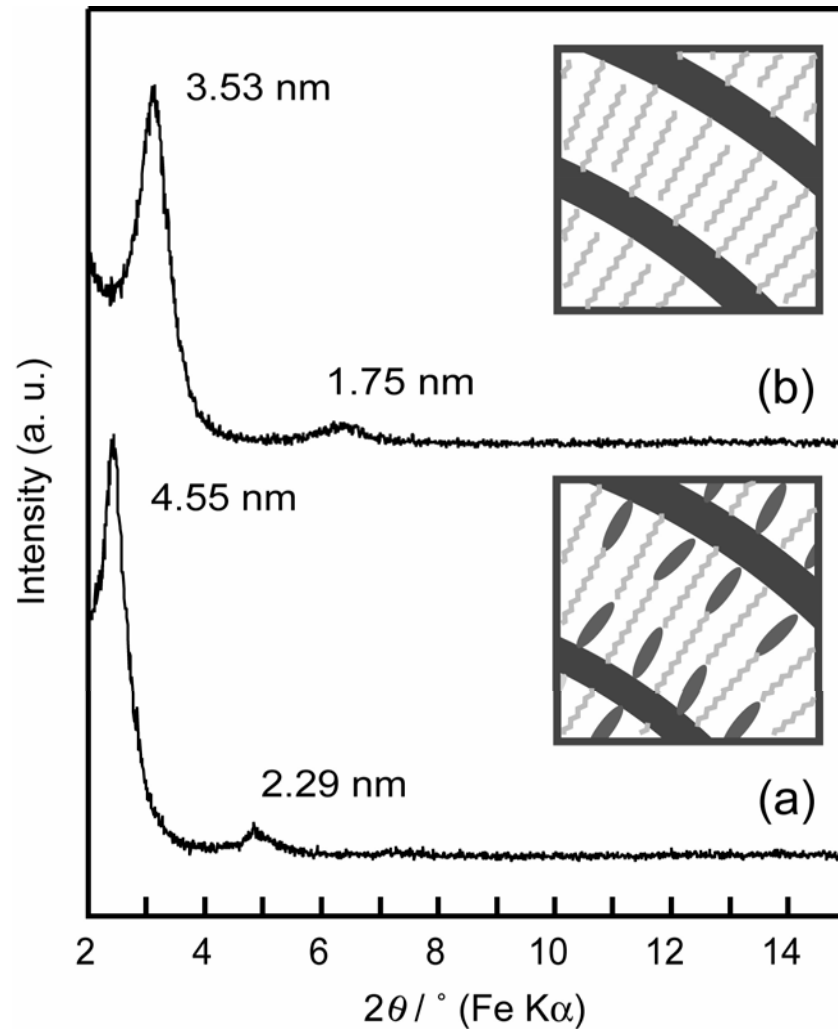


$n = 10$

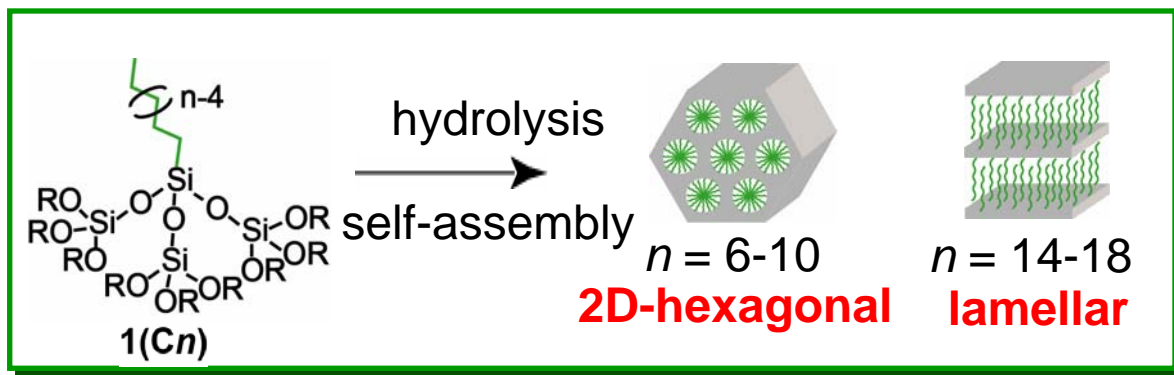


$n = 16$

Intercalation of decyl alcohol

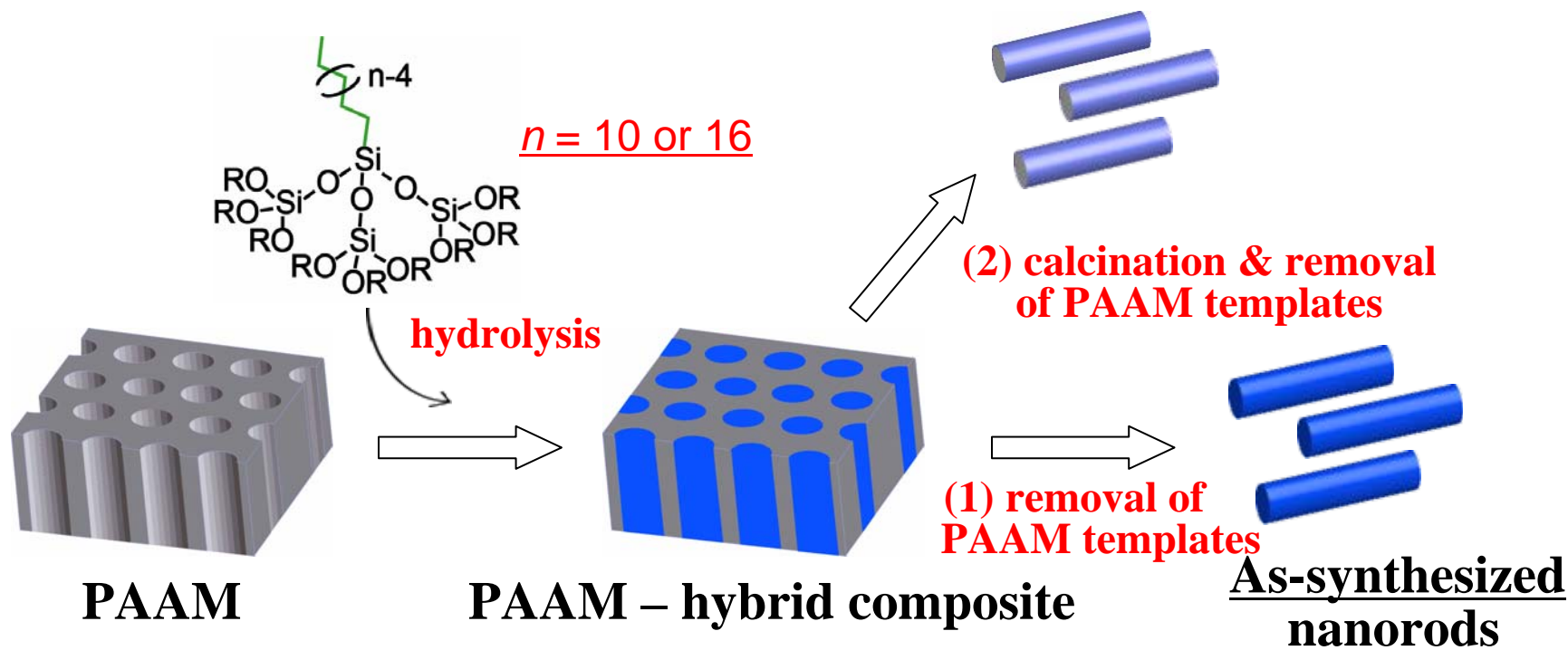


Synthesis of Siloxane-Organic Hybrid Nanorods

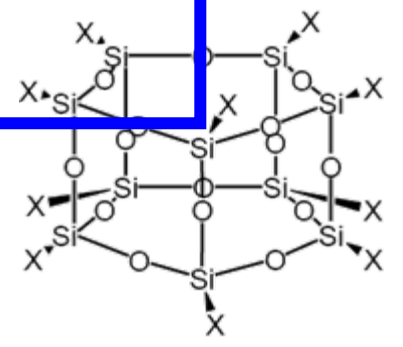
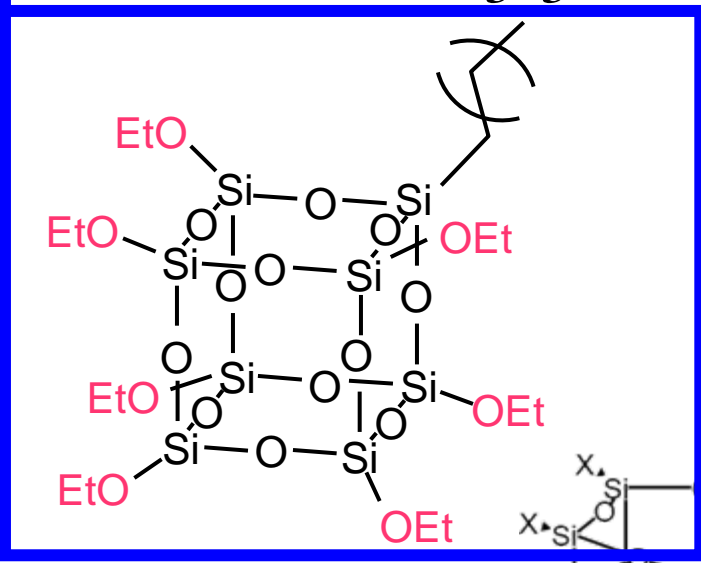
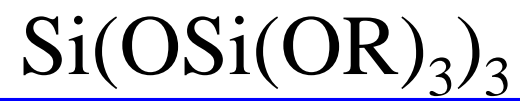
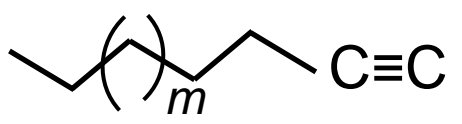
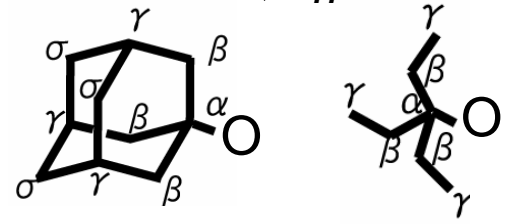
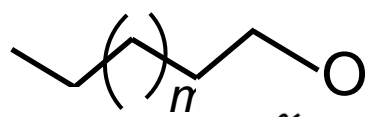
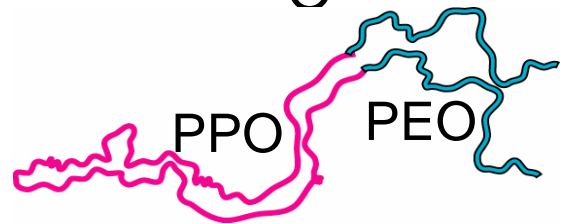
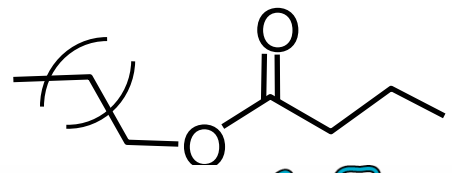
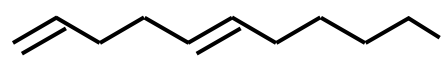
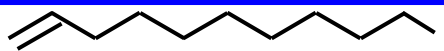
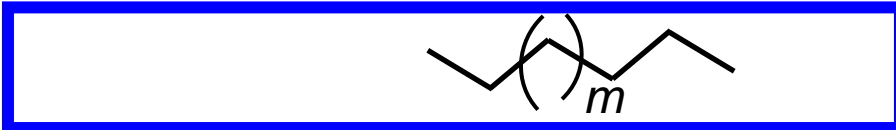


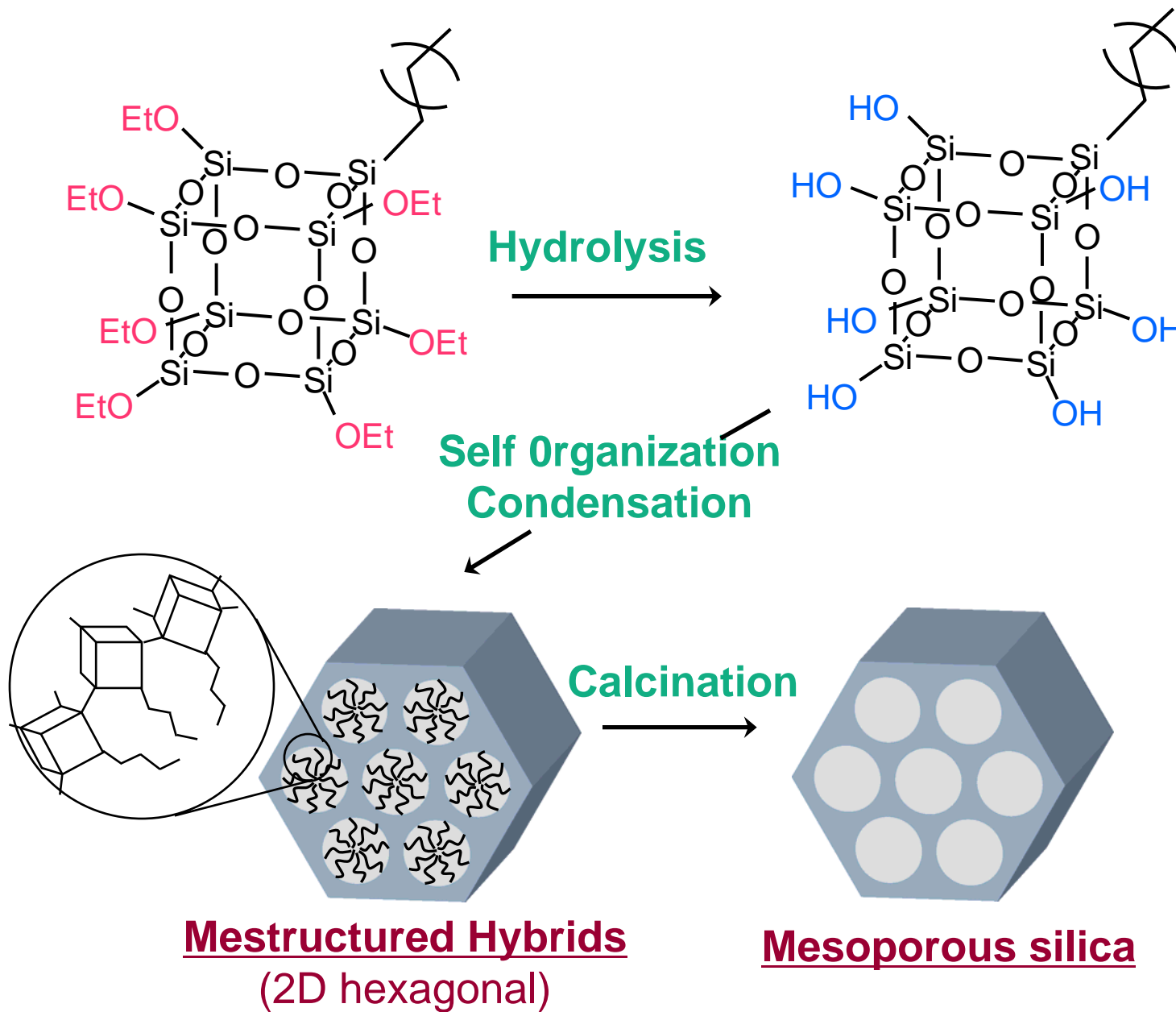
A. Shimojima et al., *J. Am. Chem. Soc.*, **127**, 14108 (2005).

Calcined nanorods

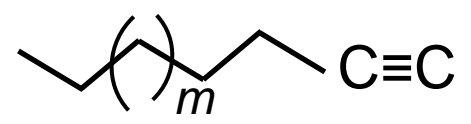
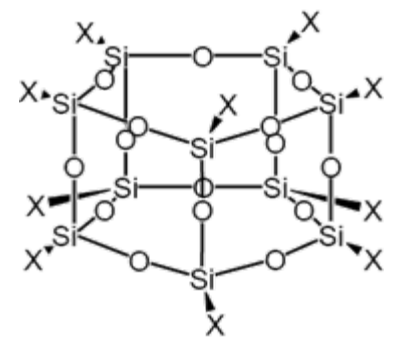
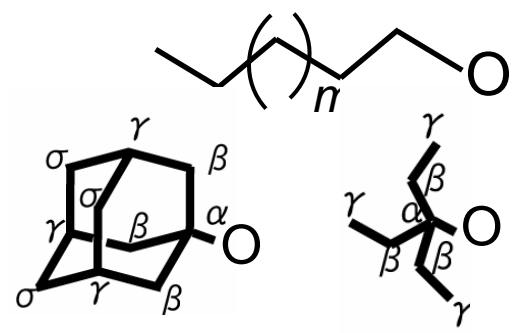
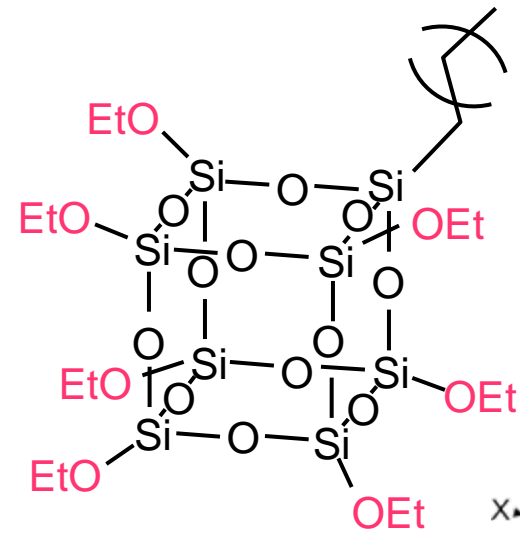
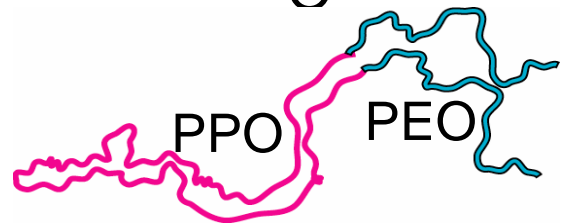
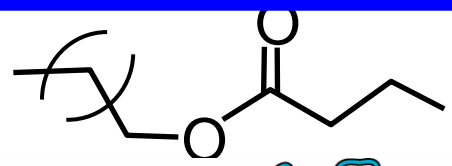
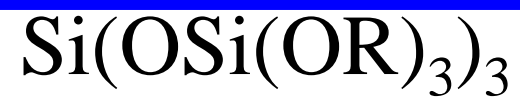
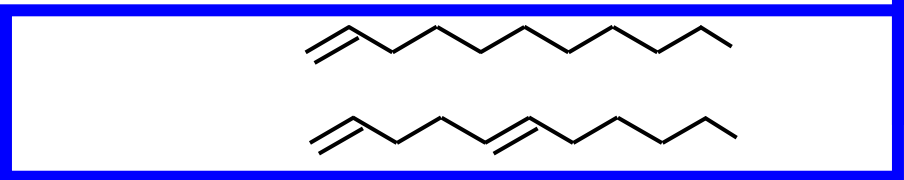


Varieties in organosilanes



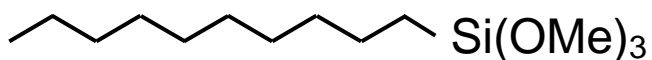


Varieties in organosilanes

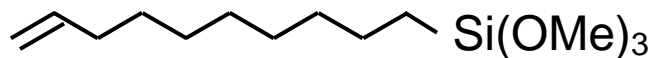
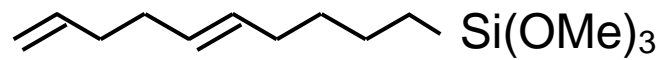


This study

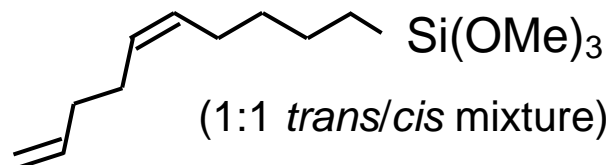
Modification of the structure and properties of multilayered hybrids by incorporating C=C double bonds



0



1



2

Co-hydrolysis and polycondensation
with $\text{Si}(\text{OMe})_4$

Multilayered films (L0, L1, L2)

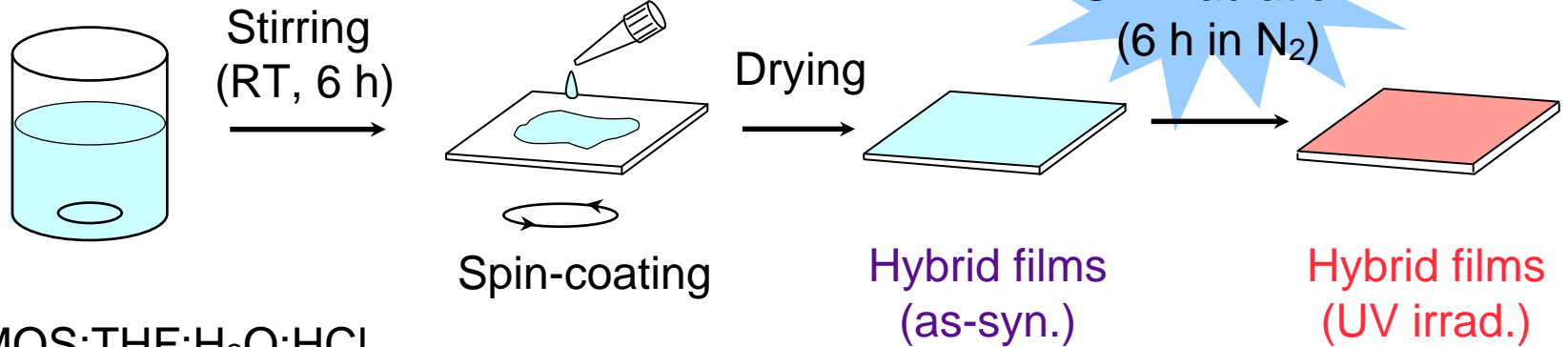
Disordered films (D1, D2)

The **Structure**, **Reactivity**, and **Properties** of the films are studied.

→ Understanding of the structure–property relationships

Experimental

Film preparations

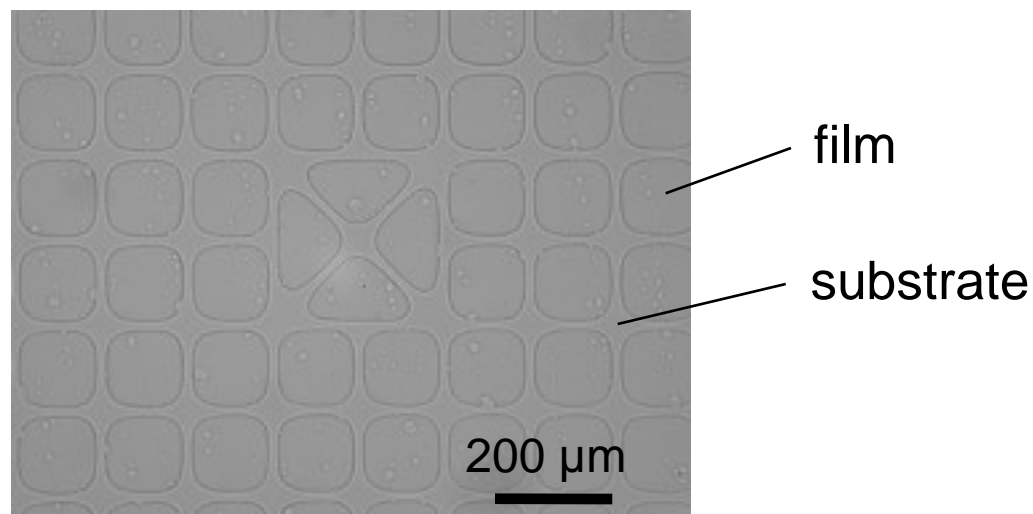
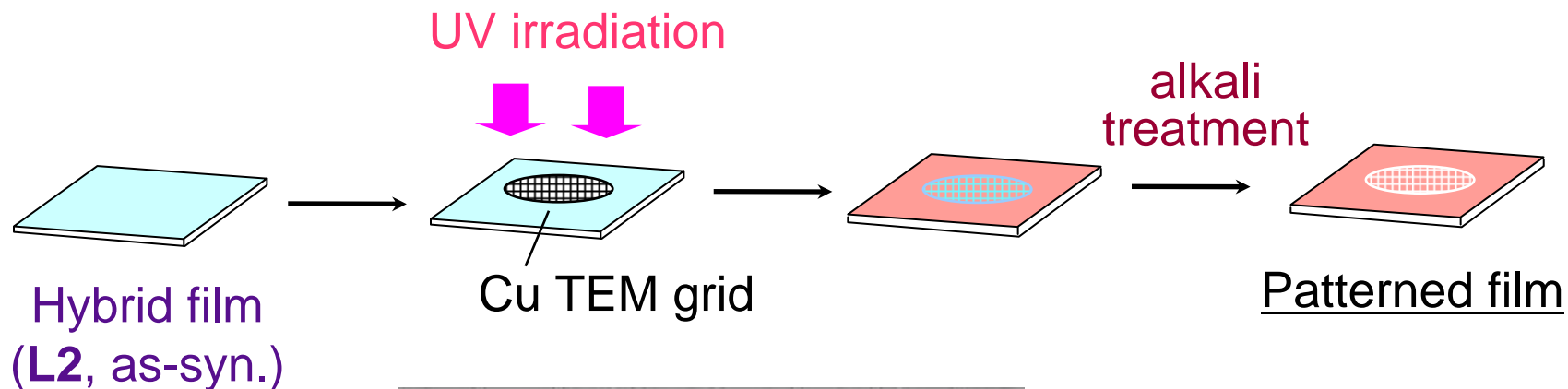


0-2:TMOS:THF:H₂O:HCl
= 1:4:15:19:0.002 (**L0**, **L1**, **L2**)
= 1:4:15:19:0.2 (**D1**, **D2**)

Analyses

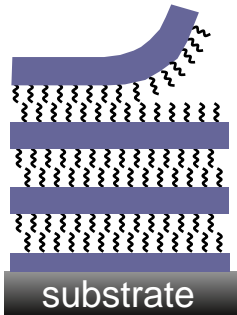
²⁹Si NMR, XRD, IR, TEM, SEM, Nanoindentation test

Micropatterning



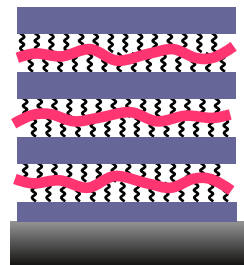
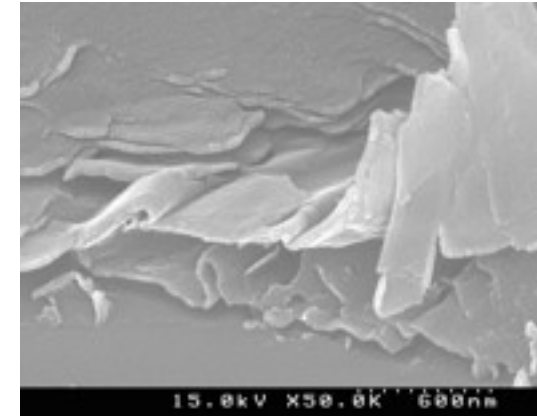
Such patterning was not achieved by using disordered films (**D1** and **D2**).

Structure–property relationships



L0, L1, L2 (as-syn.)

✗ Hardness ✗ Alkali resistance
No covalent bonds between adjacent layers (easily delaminated)

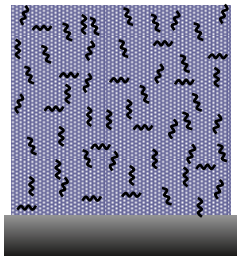


L1, L2 (UV irradi.)

⊙ Hardness ○ Alkali resistance

All of the layers are linked by covalent (Si-O, Si-C, and C-C) bonds

Each siloxane layer is sandwiched by polymer layers (protected from being etched by alkali solutions)

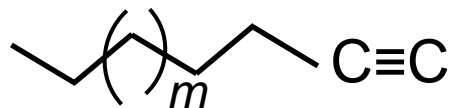
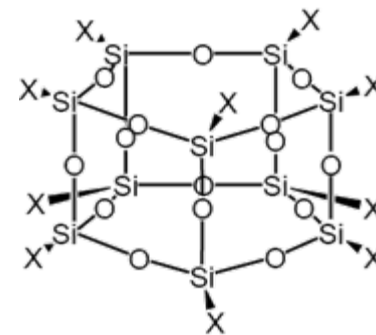
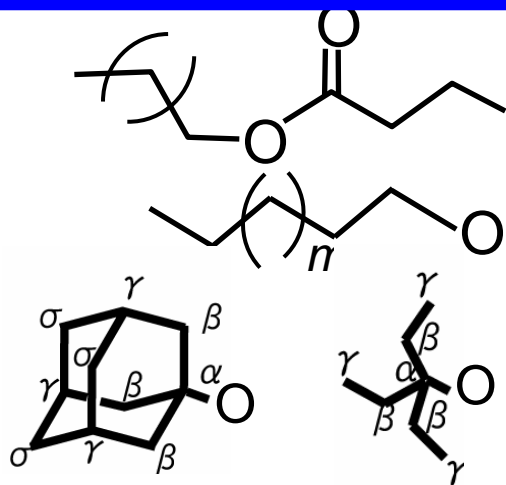
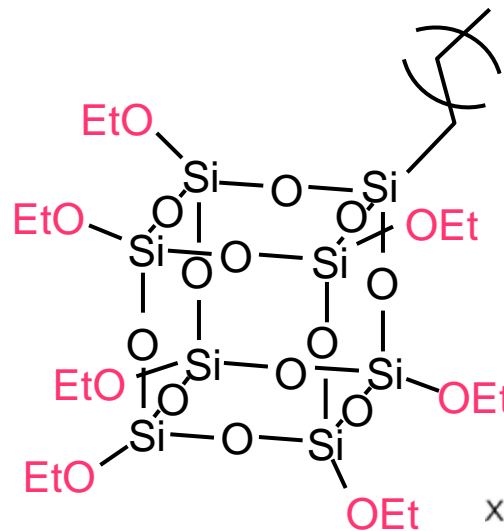
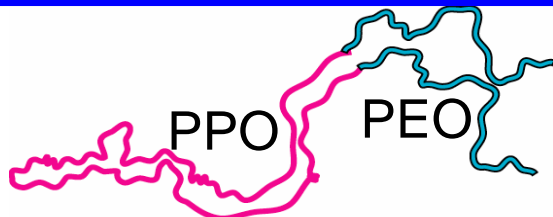
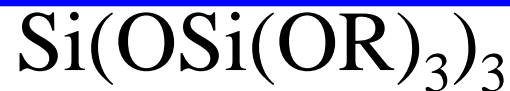
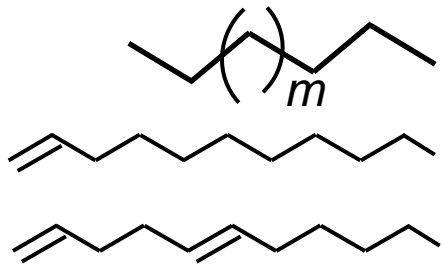


D1, D2

○ Hardness △ Alkali resistance

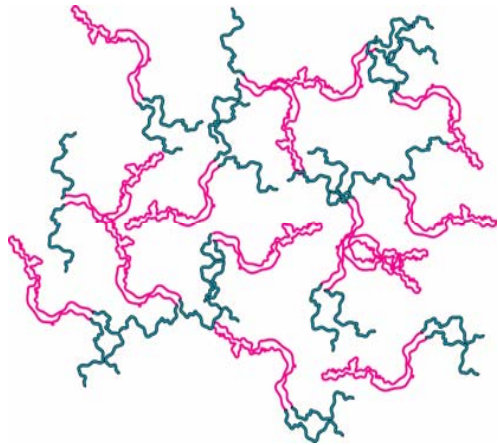
Three-dimensional, isotropic siloxane networks
Easily etched by alkali hydrolysis of Si-O-Si bonds

Varieties in organosilanes

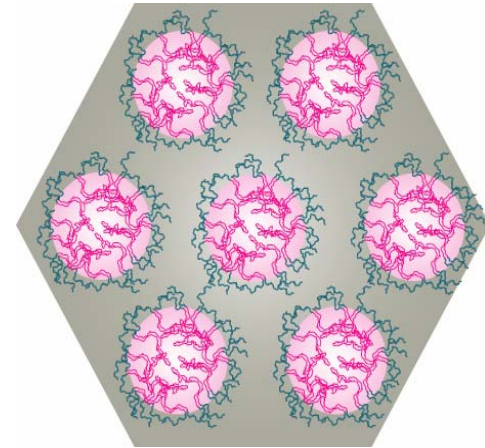


Structural design using inorganic and organic units

Supramolecular templating method

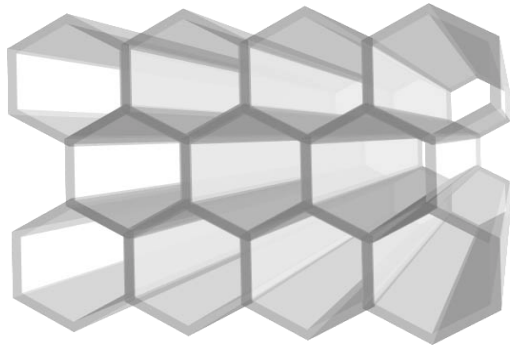


Self-assembly
+ Inorganic species



Mesostructured materials

Mesoporous silicas

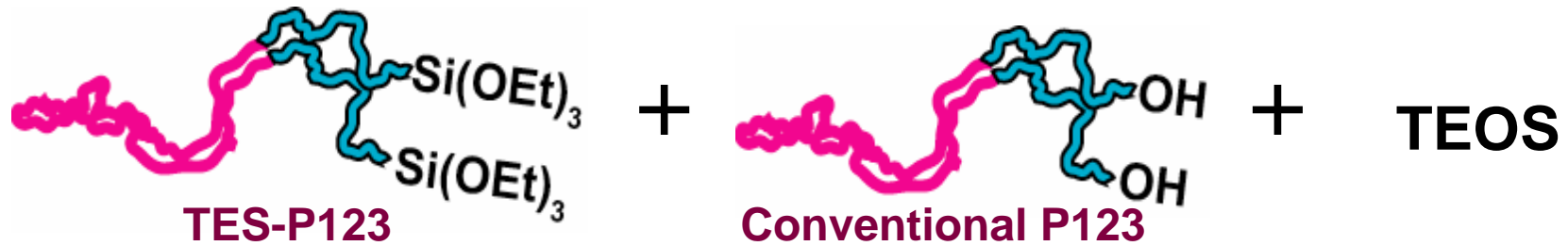


SBA-15

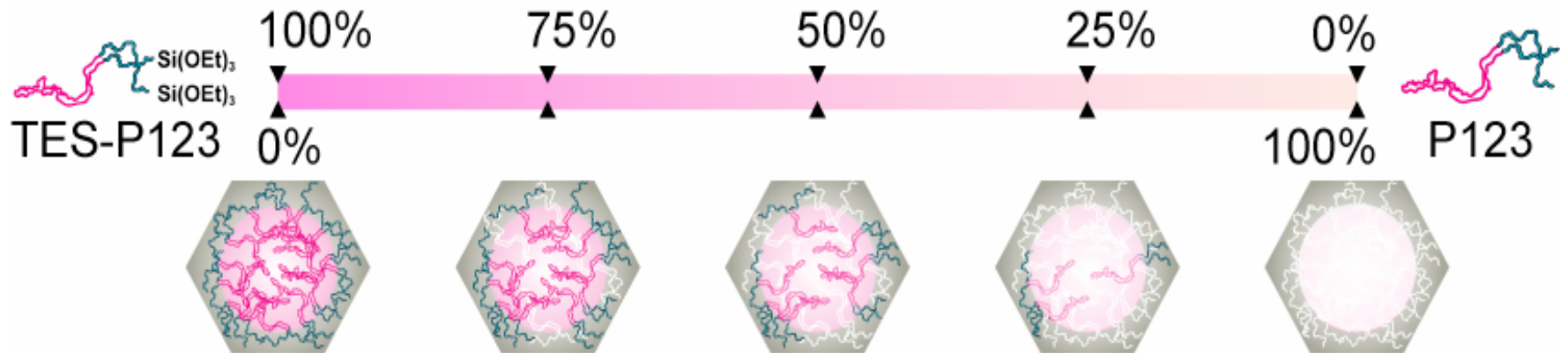
- Homogeneous mesopores
- Well-ordered porous-nanostructures
- High specific surface areas
- Open pore
- Biocompatibility

Large mesopores
Hydrothermal stability

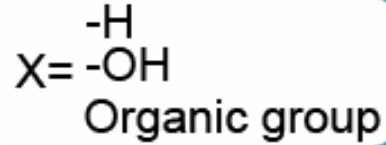
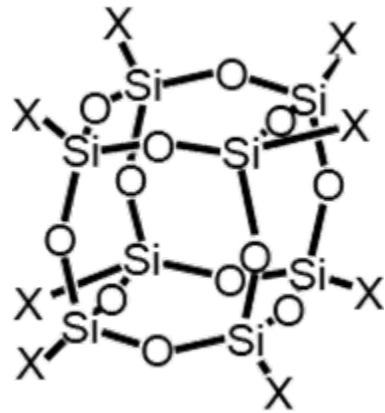
Control of the amount of P123 within mesopores



Selective removal of conventional P123



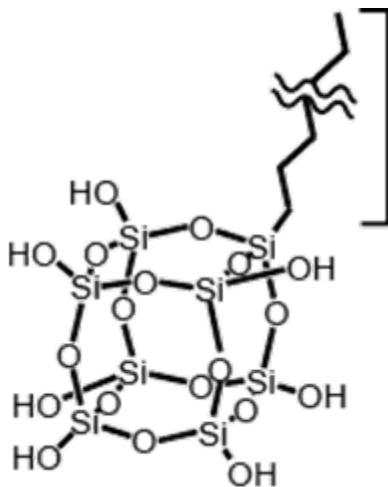
Incorporation of cage-type siloxane units (D4R) units into mesostructured materials



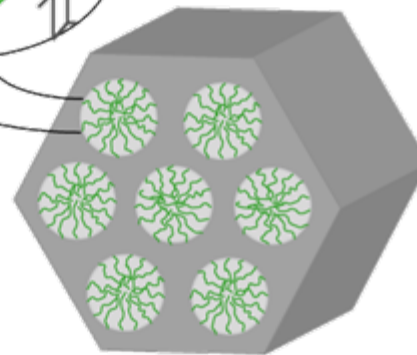
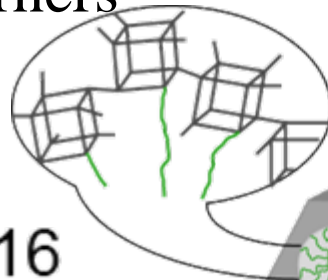
D4R units

- one of building units for zeolites
- symmetrical
- bonding with various organic groups on the

corners



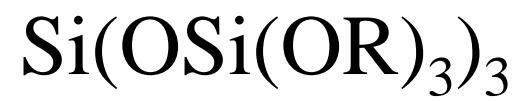
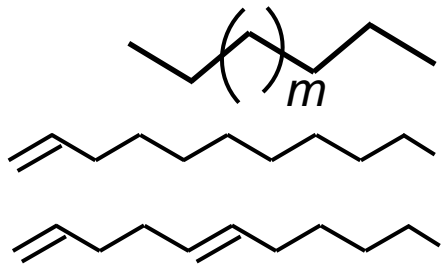
C16



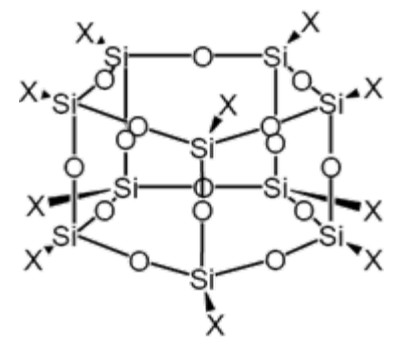
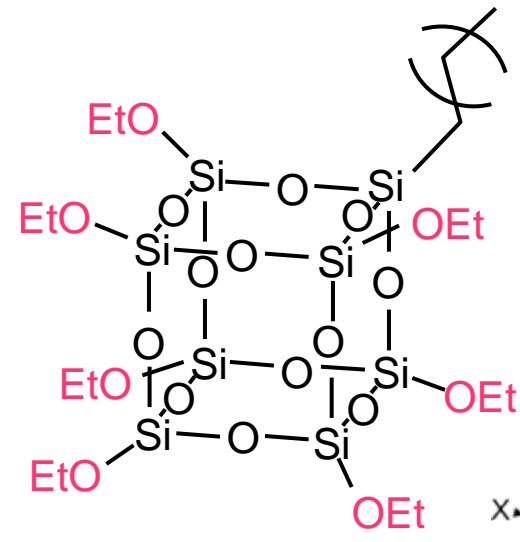
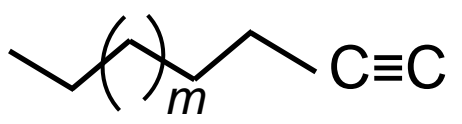
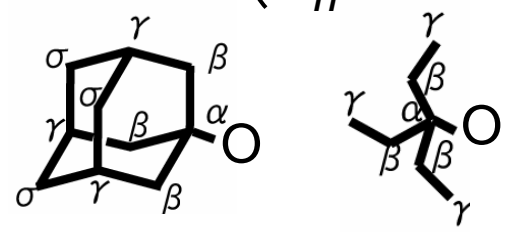
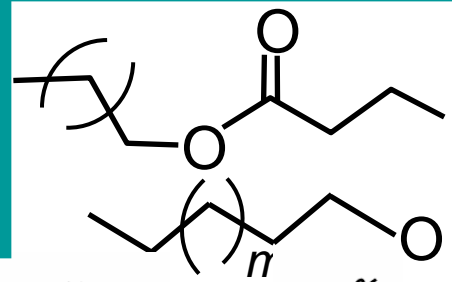
Calcination

Calcination for removal of C16 groups
→ Possible degradation of D4R units

Varieties in organosilanes



Chemically
Cleavable
Groups



Alkoxychlorosilanes

Alkoxychlorosilanes $(\text{RO})_n\text{SiCl}_{4-n}$

**Different reactivities of
alkoxy groups and chloro groups**

Grafting with chloro groups

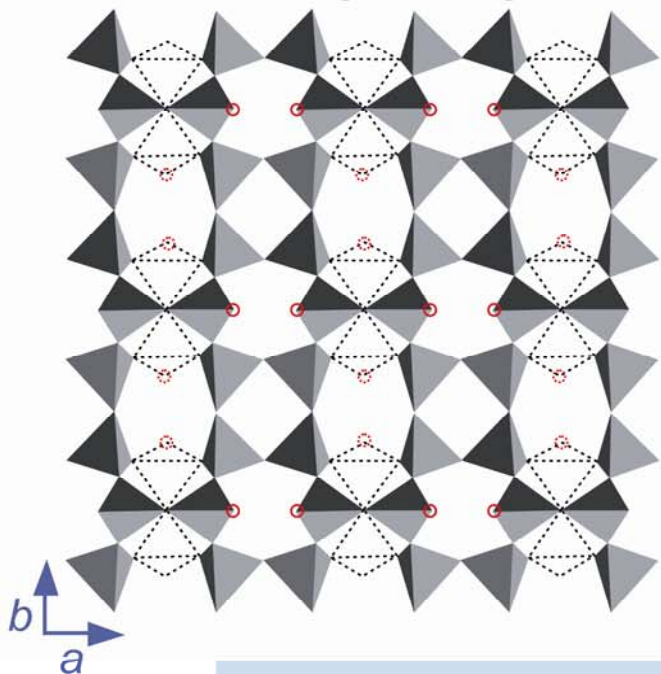
Incorporation of SiO_4 units into(onto) silicates

Soft chemical removal of alkoxy groups by hydrolysis

Silylation of octosilicate

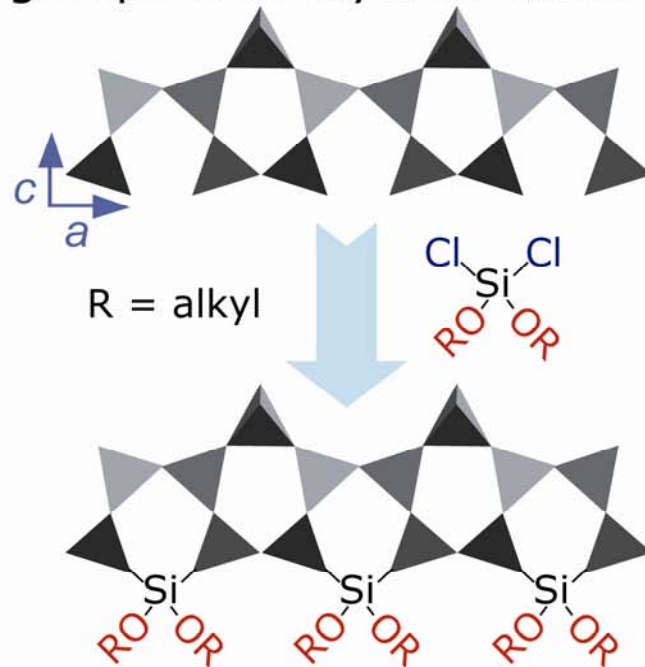
Octosilicate

- Stable Silicate Structure
- Large Difference of the Distances among SiOH and/or SiO⁻ Sites along Orthogonal Axes

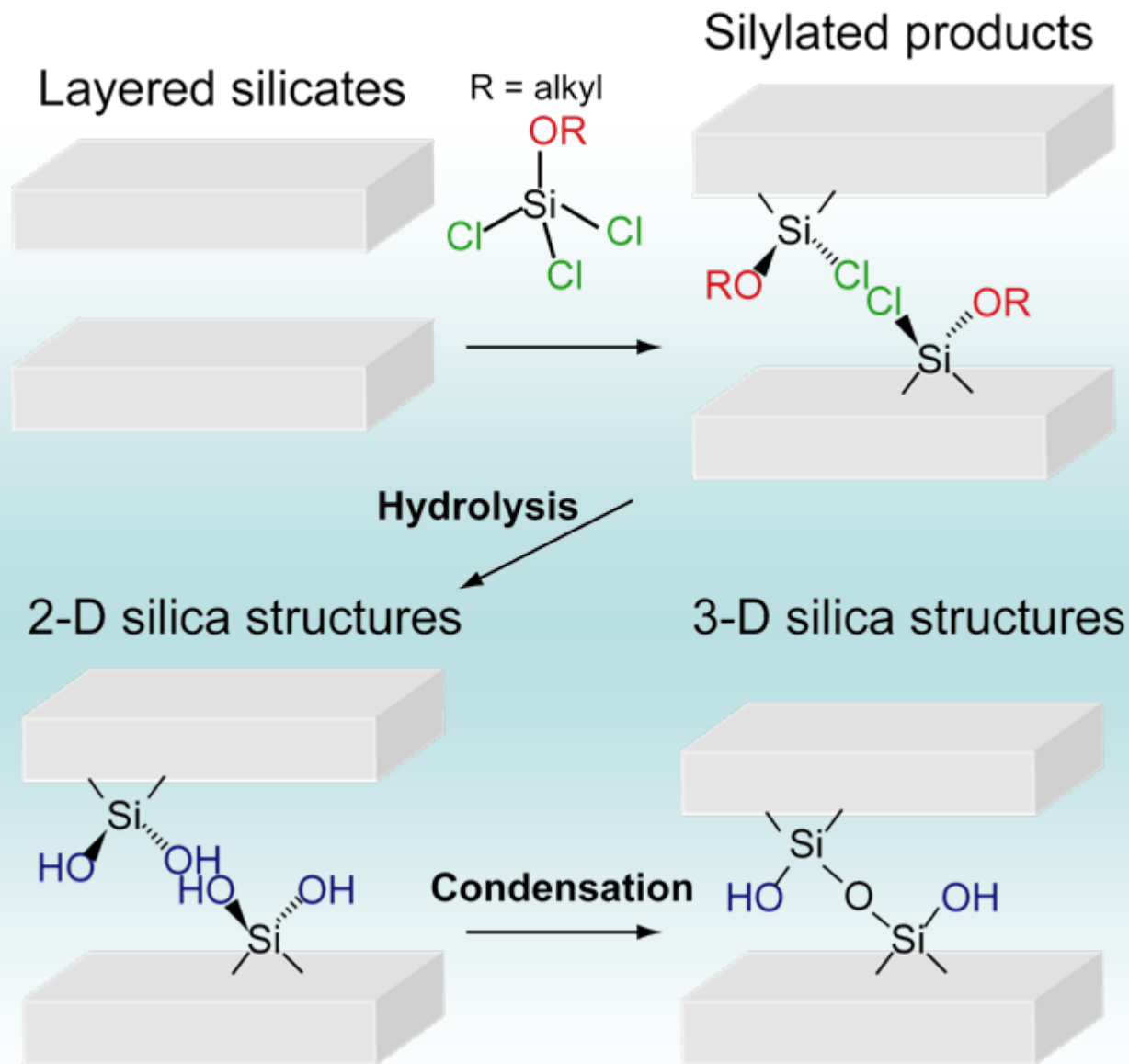


Silylation of Octosilicate with Dialkoxydichlorosilanes

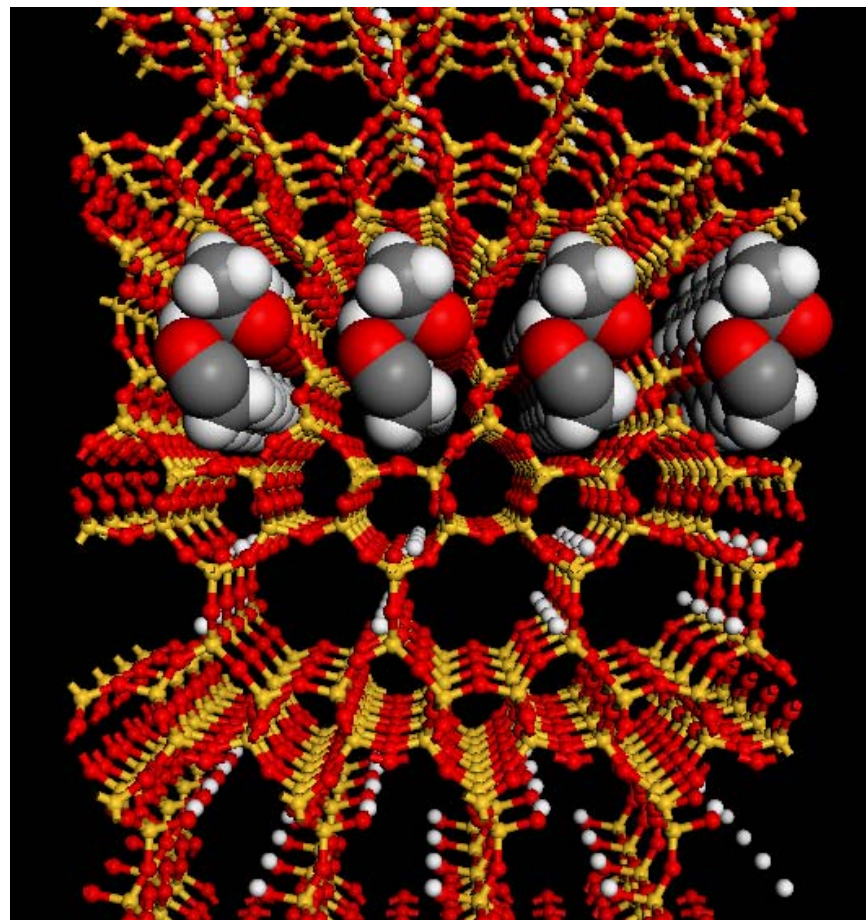
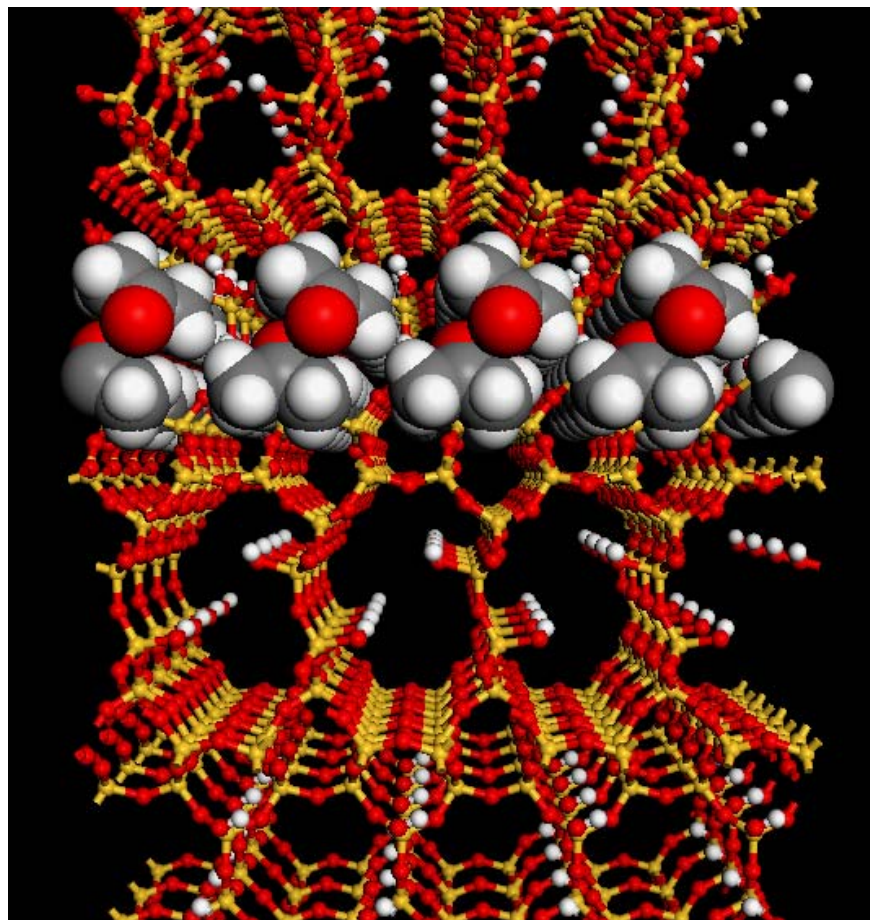
Controlled grafting of dialkoxysilyl groups onto layered silicate



Formation of Novel Molecularly Ordered Alkoxysilylated-Derivatives of Layered Silicate



Design of silica 2-D or 3-D nanostructures using alkoxylation and subsequent hydrolysis



Mochizuki, Shimojima, Kuroda, JACS (2005)

Lots of opportunities in materials chemistry

