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Waseda University, Japan

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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

Kazuyuki Kuroda

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Kagami Memorial Laboratory for Materials Science & Technology, Waseda University
CREST, Japan Science and Technology Agency

OUTLINE

Background

Mesoporous materials

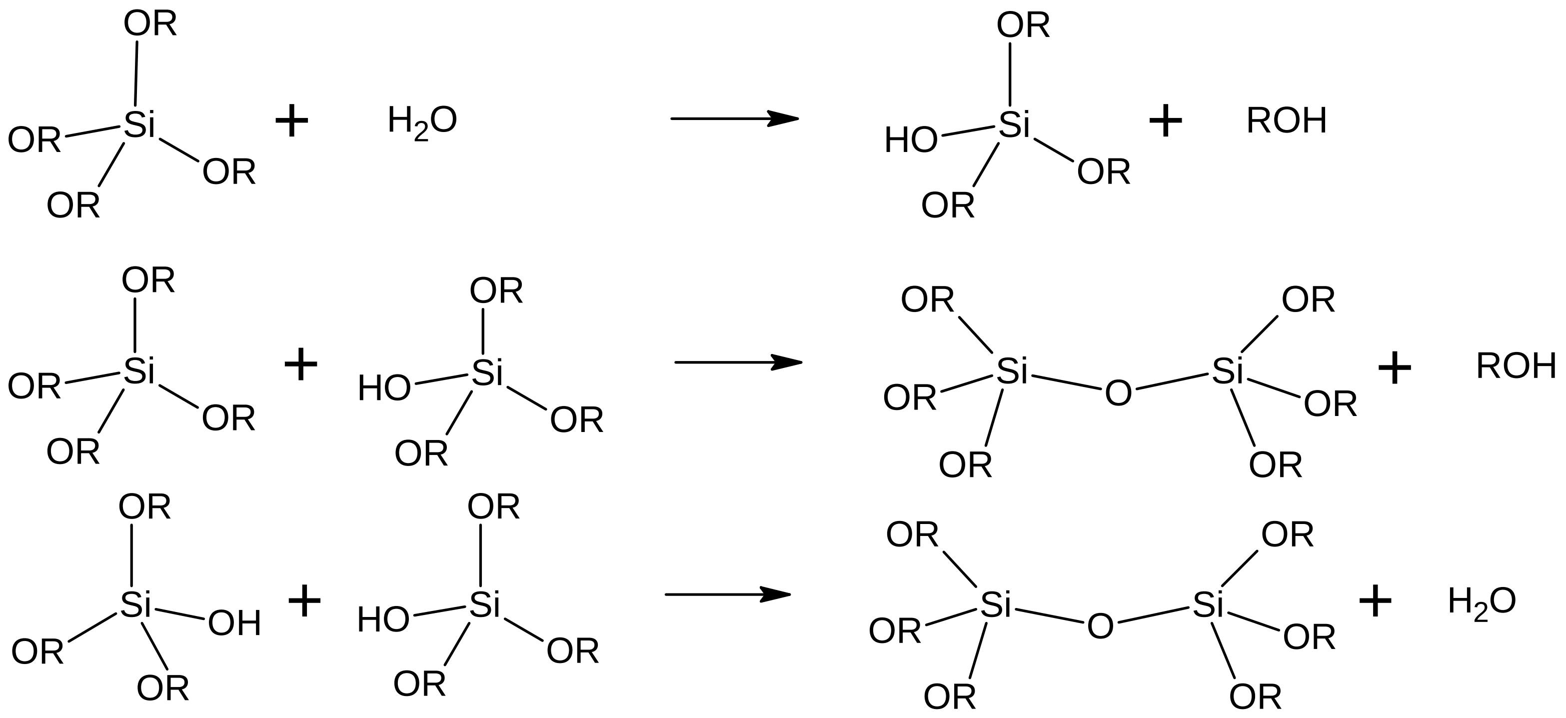
Mesoporous films utilizing alkoxysilanes

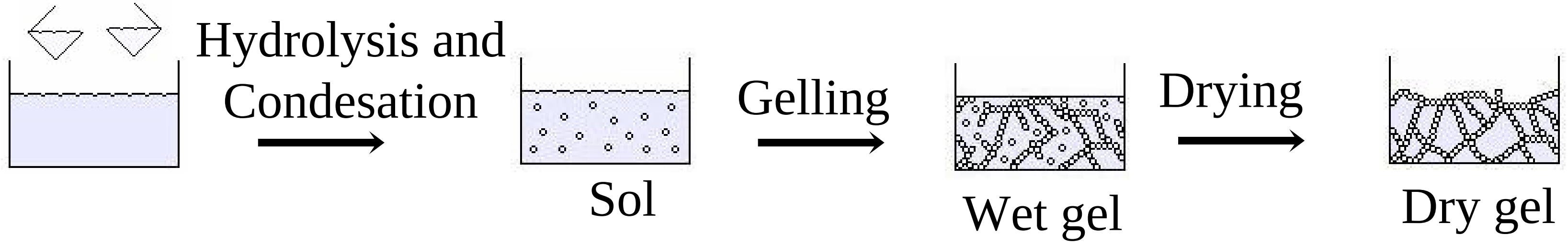
Design of alkoxysilanes and self-assembly

Varieties and possibilities

SOL-GEL Process

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





Hydrolysis and Condensation

Sol

Gelling

Wet gel

Drying

Dry gel

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

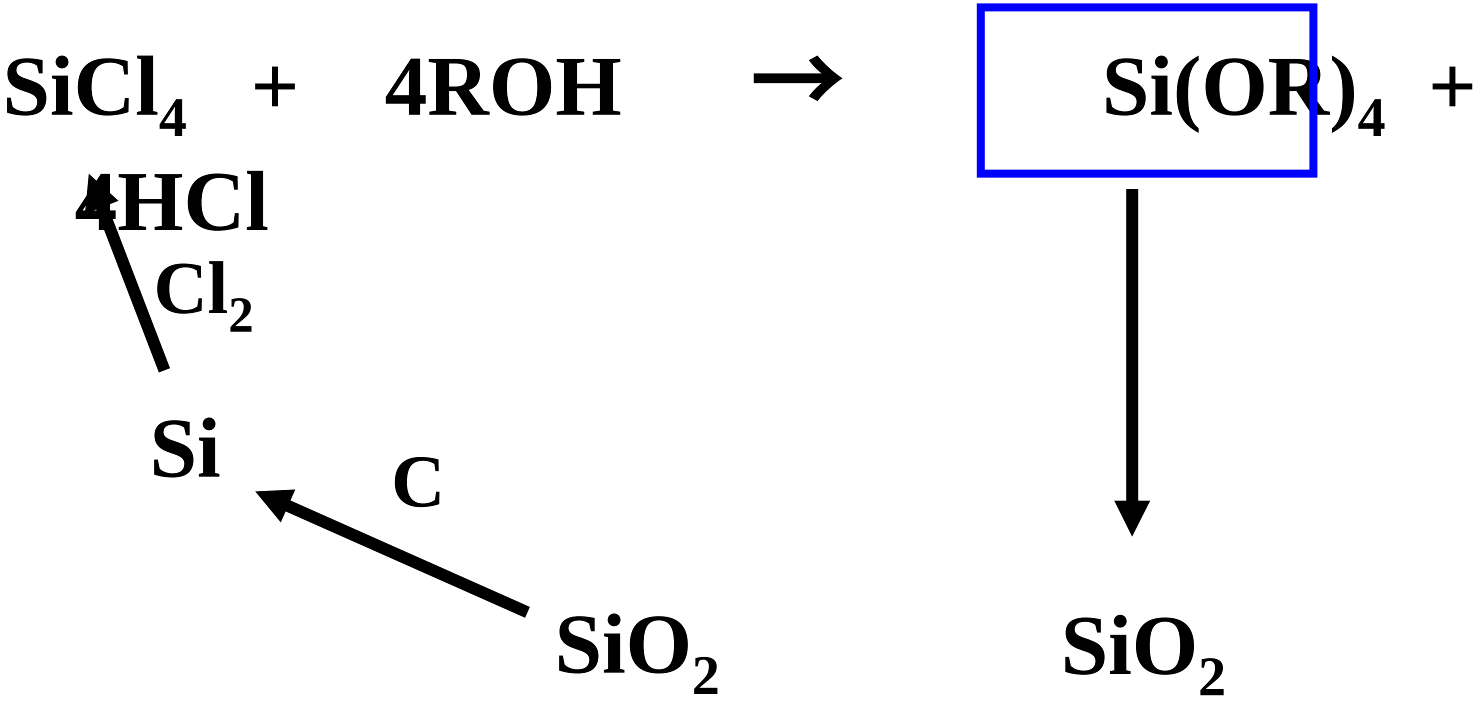
Tetraalkoxysilanes $Si(OR)_4$

R= CH_3 (b.p. 121 ^oC) ,
C_2H_5 (b.p. 169 ^oC), etc.

Well defined monomeric SiO_4 unit

Reactivity of alkoxy groups
(hydrolysis and condensation)

Synthesis of tetraalkoxysilane



$SiCl_4 + 4ROH \rightarrow \boxed{Si(OR)_4} + 4HCl$

Cl_2

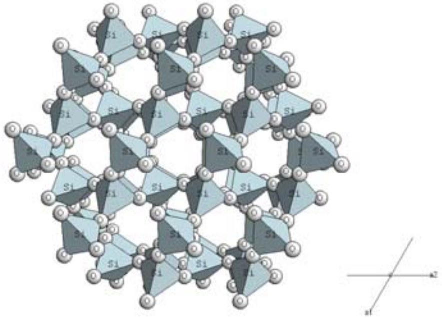
Si

C

SiO_2

SiO_2

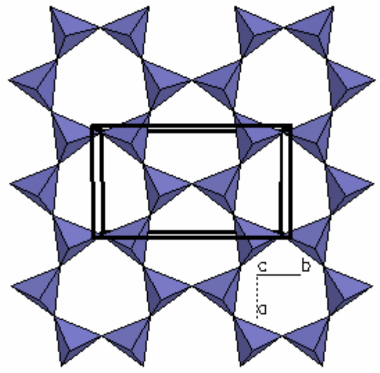
Si-O system: from Lattice to Molecules



3D Lattice:

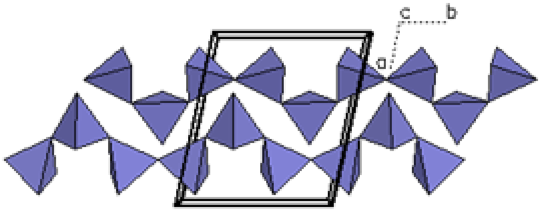
SiO_2 (Quartz, Cristobalite,….)

zeolites and mesoporous silica



2D Lattice:

layered silicates (Mica, Kaolinite…….)



1D Lattice:

chain silicates (pyroxene, ……)

Clusters

$Si_8O_{20}{}^{8-}$ ………………….

Molecules:

$Si(OC_2H_5)_4$,$Si(OH)_4$ ……………

OUTLINE

Background

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Design of alkoxysilanes and self-assembly

Varieties and possibilities

Nanoporous Materials

gas storage materials

materials with low dielectric constants

photocatalytic materials

materials with low refractive indices

adsorbents

biological and biomedical applications

green chemistry

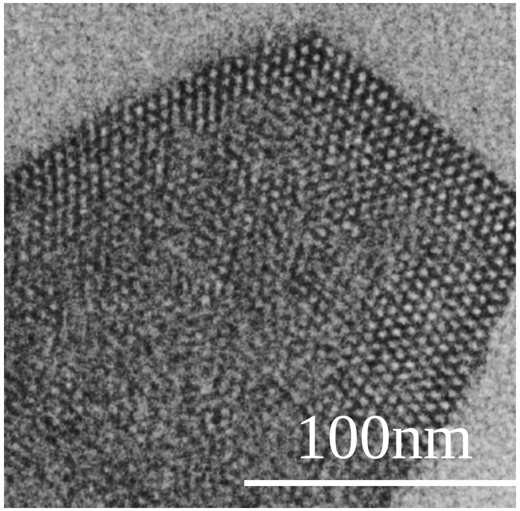
catalysts

catalyst supports

reactions in confined space

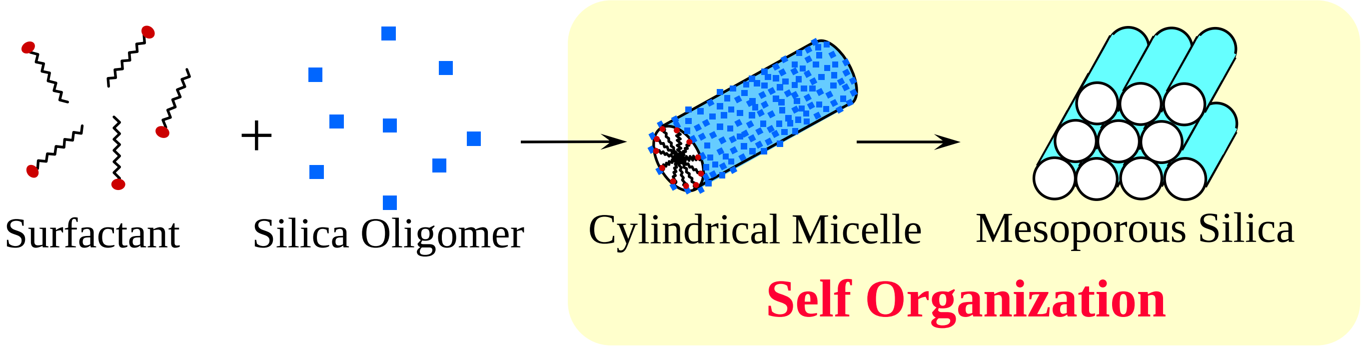
Design of Novel Porous Materials at a nanometer scale

Mesoporous Materials



Regularly Arranged Mesopores (Pore: 2 ~ 50 nm)

Supramolecular Templating (Surfactant Micelles)



Surfactant + Silica Oligomer → Cylindrical Micelle → Mesoporous Silica

Self Organization

1. Mesophases

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

2. Pore Sizes

   Alkyl Chain Length of Surfactant, Expander Molecules

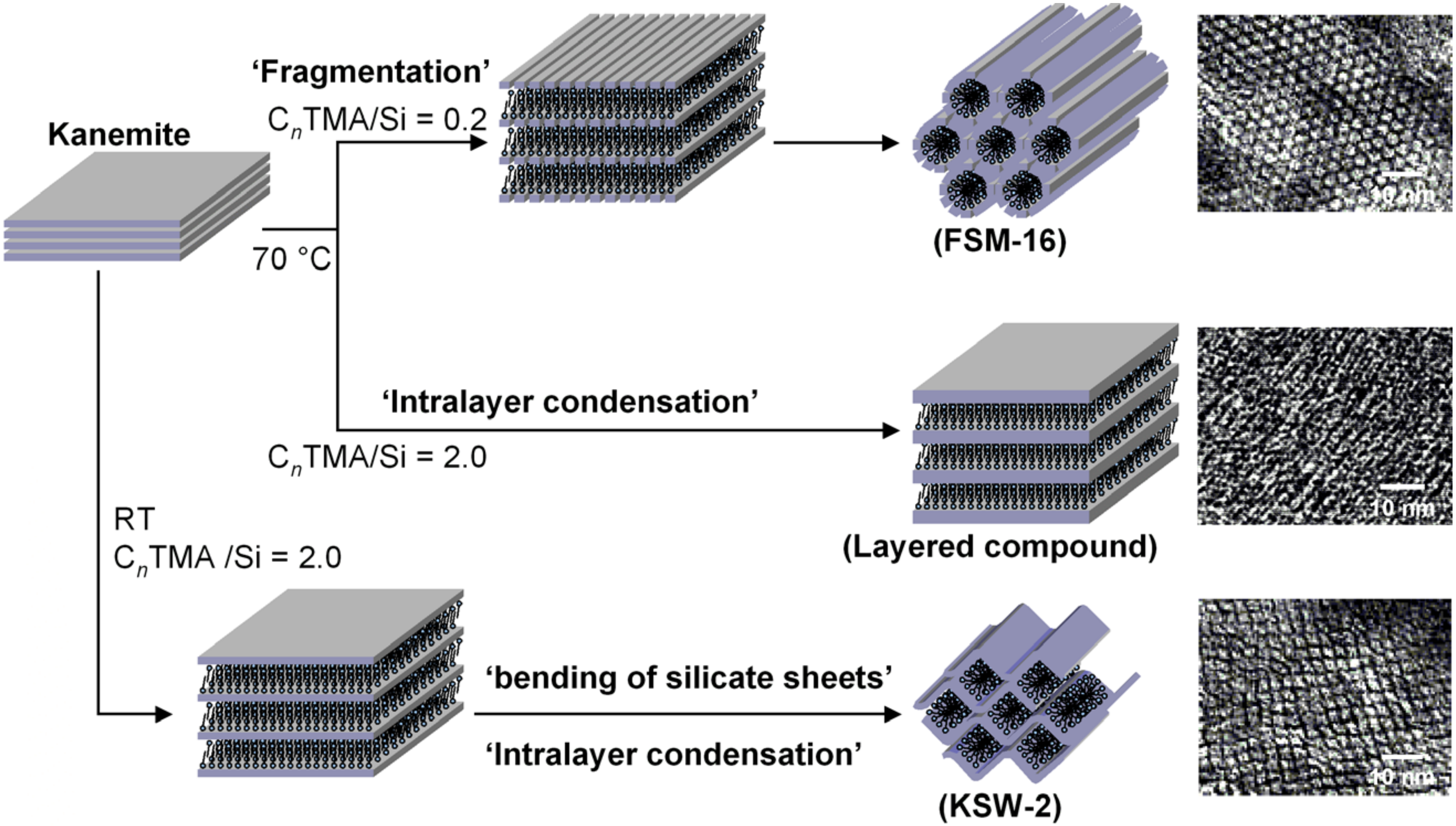
   Non-ionic Surfactants

3. Wall Composites

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

4. Macroscopic Morphologies

   Particle, Film, Sphere, Fiber, Monolith



Kanemite

'Fragmentation'

$C_nTMA/Si = 0.2$

70 °C

(FSM-16)

10 nm

'Intralayer condensation'

$C_nTMA/Si = 2.0$

(Layered compound)

10 nm

RT

$C_nTMA /Si = 2.0$

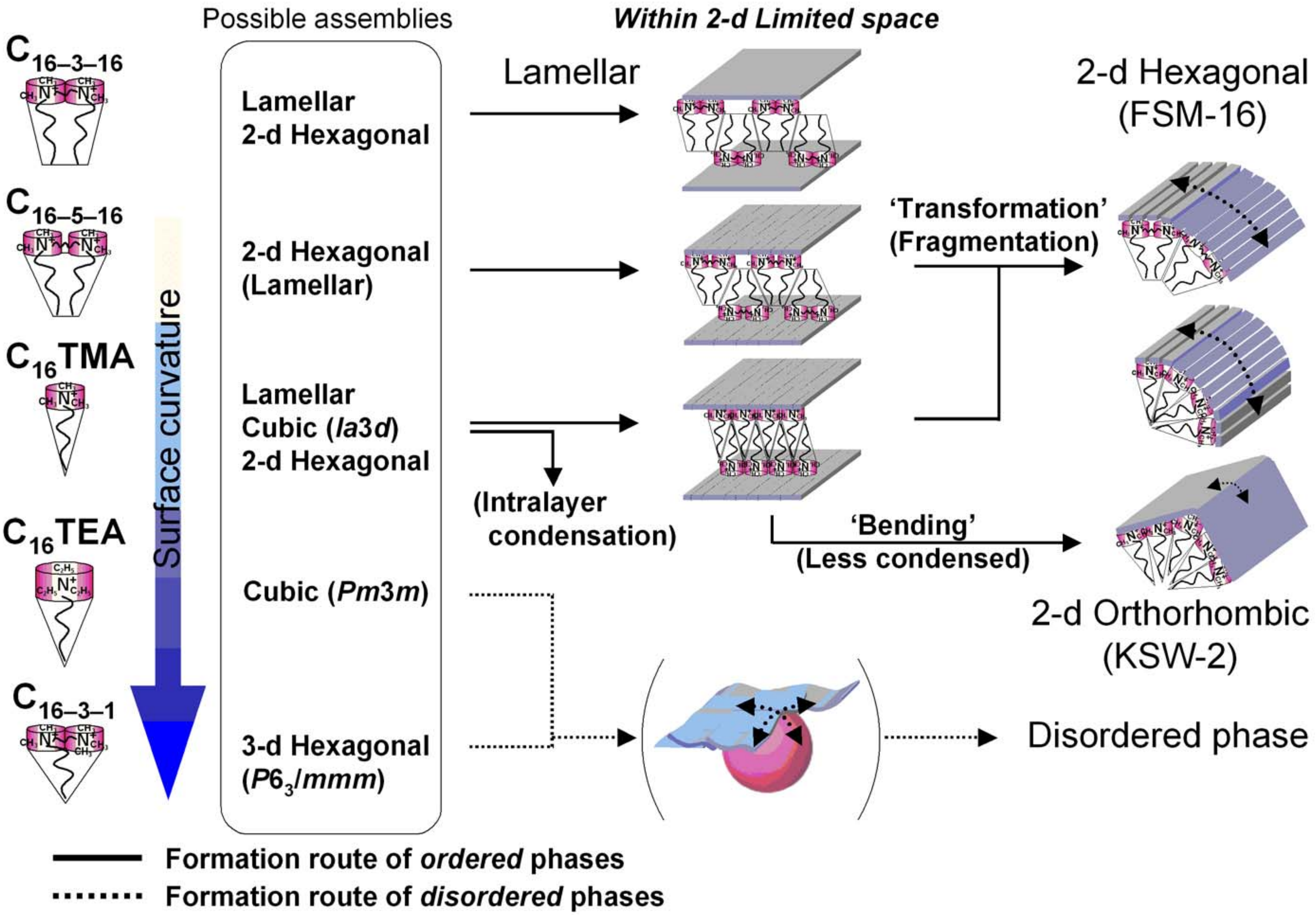
'bending of silicate sheets'

'Intralayer condensation'

(KSW-2)

10 nm

T. Kimura et al., *Bull. Chem. Soc. Jpn.* (2004)



T. Kimura, D.Itoh, T. Shigeno, K. Kuroda, *Bull. Chem. Soc. Jpn.*, **77**, 585(2004)

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,
……………………

OUTLINE

Background

Mesoporous materials

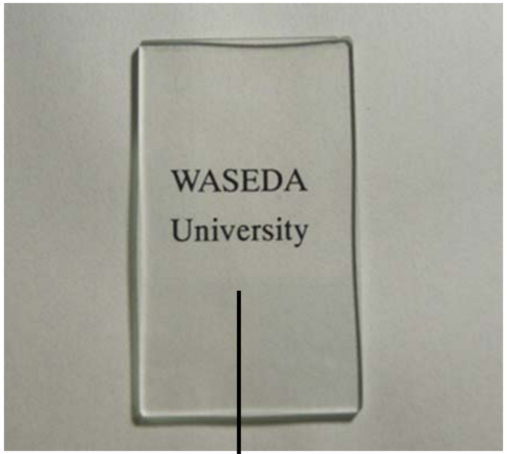
<u>Mesoporous films utilizing alkoxysilanes</u>

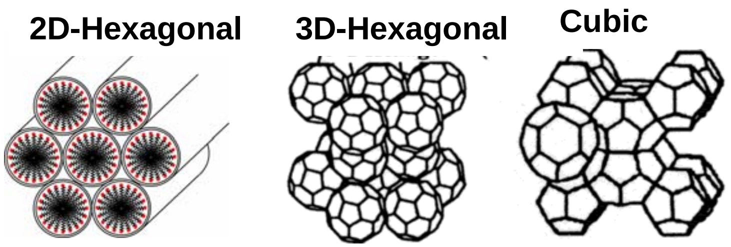
Design of alkoxysilanes and self-assembly

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**



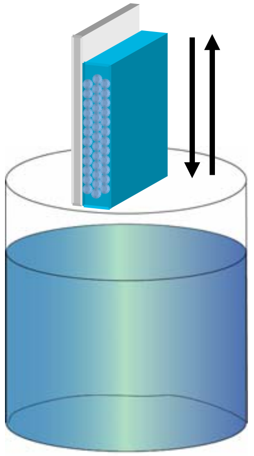


Various Mesostructures

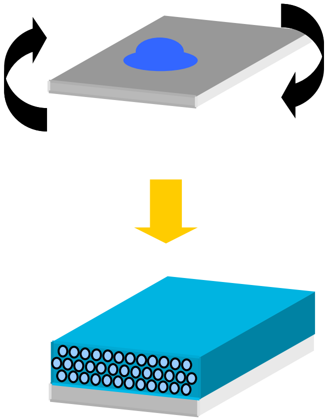
Optical, Electronic, and Molecular Devices,
Low-*k* Dielectrics, Photocatalysts, Sensors,
Biomedical, …

Synthetic methods

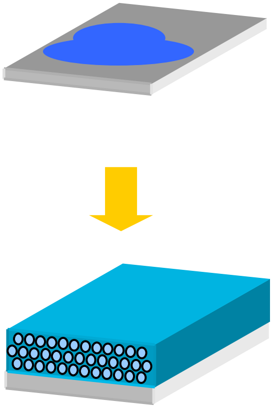
- EISA (Evaporation Induced Self-Assembly)



Dip-Coating



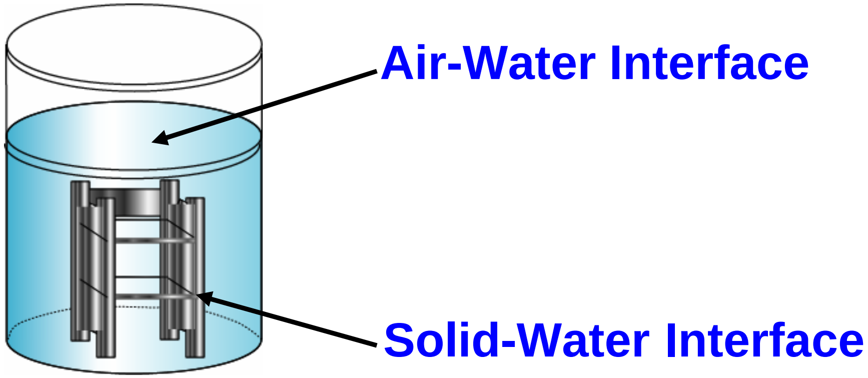
Spin-Coating



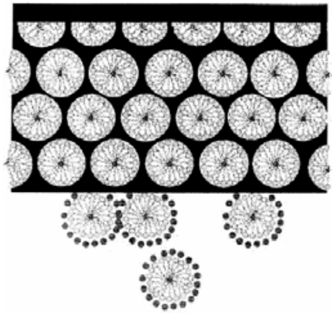
Casting

- Hydrothermal Synthesis

(Heterogeneous Nucleation and Growth)



Model[a]

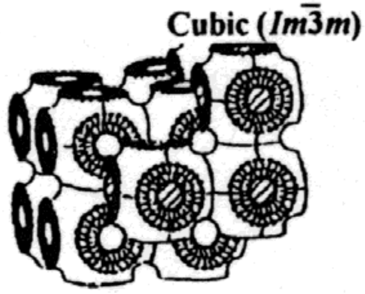


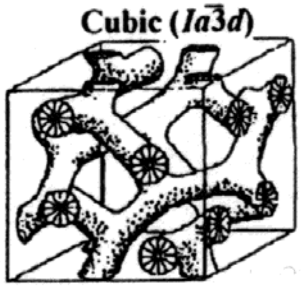
a) H.Yang, G. A. Ozin, *Nature*, **1996**, 379, 703.

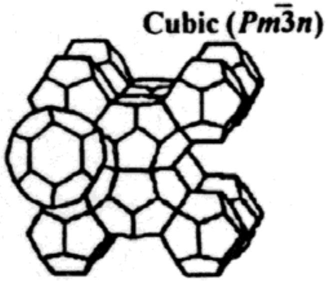
Mesoporous Silica Films

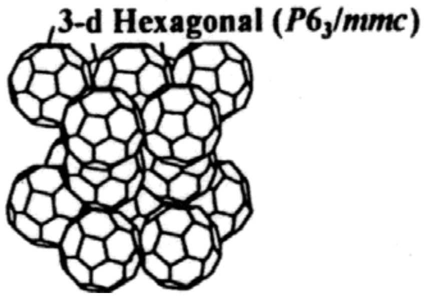
Various Mesostructures, Conditions

- *Pm3n, Im3m* (P123[a], F127[a], CTEABr[b])
- *Lamellar* (SDS[c], Anionic Surfactant)
- $P6_3/mmc$ (CTAB[d,e])
- *Ia-3d* (Brij56[f])
- *R3m* (P123[g])
- *p6mm* (Basic Condition[h])


Cubic ($Im\bar{3}m$)


Cubic ($Ia\bar{3}d$)


Cubic ($Pm\bar{3}n$)


3-d Hexagonal ($P6_3/mmc$)

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.

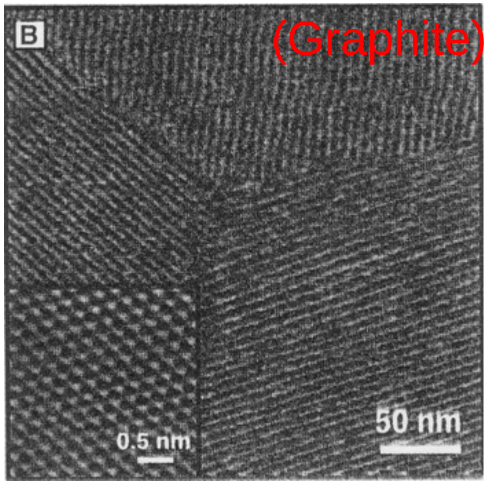
Mesoporous Silica Film (Hydrothermal)

■ Hydrothermal Synthesis

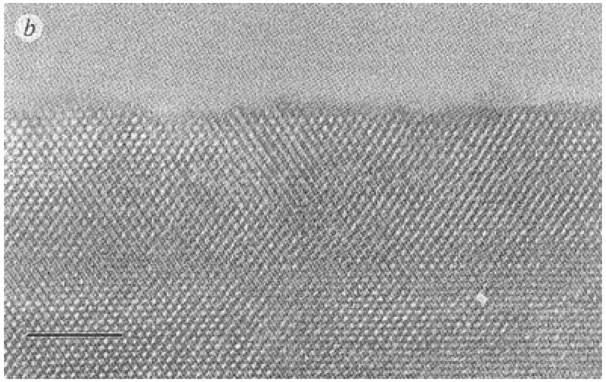
(On Mica, Graphite & Air-Water Interface, 2D-Hexagonal)

SEM[a]

AFM[c]



TEM[a]



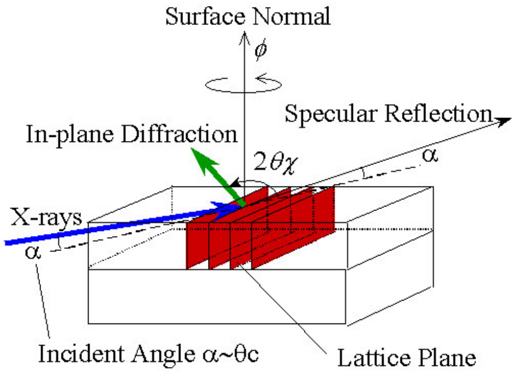
- Highly Ordered 2D-Hexagonal Mesoporous Structure
- Alignment Control of Mesochannels Reflected the Symmetry of Substrates

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

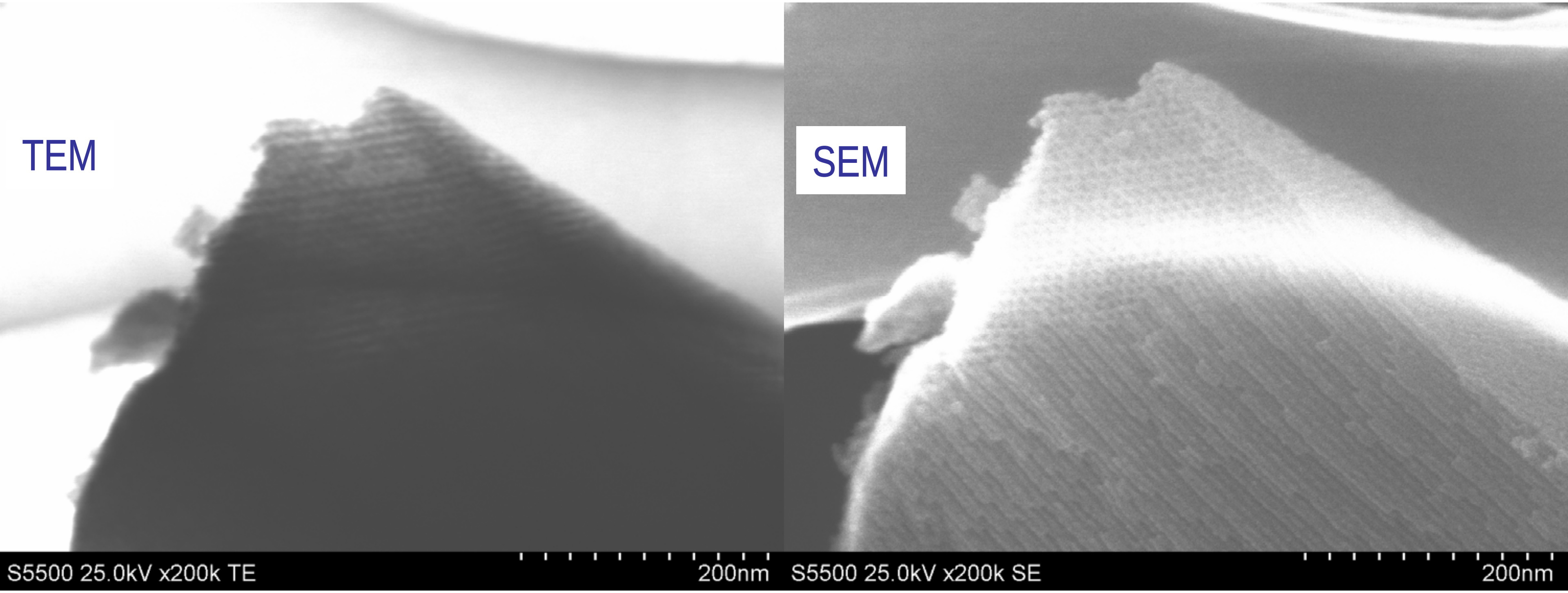
- X-Ray Diffraction (Out-Of-Plane, In-Plane, 2-Dimensional[j])
- *In-Situ* Time-Resolved Small Angle X-Ray Scattering[a-f]
- Small Angle Neutron Scattering[i]
- High Resolution Scanning Electron Microscopy (HR-SEM)[g,h]
- Transmission Electron Microscopy (TEM)
- Gas Adsorption
- Secular X-Ray Refractivity
- 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.
I) 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.

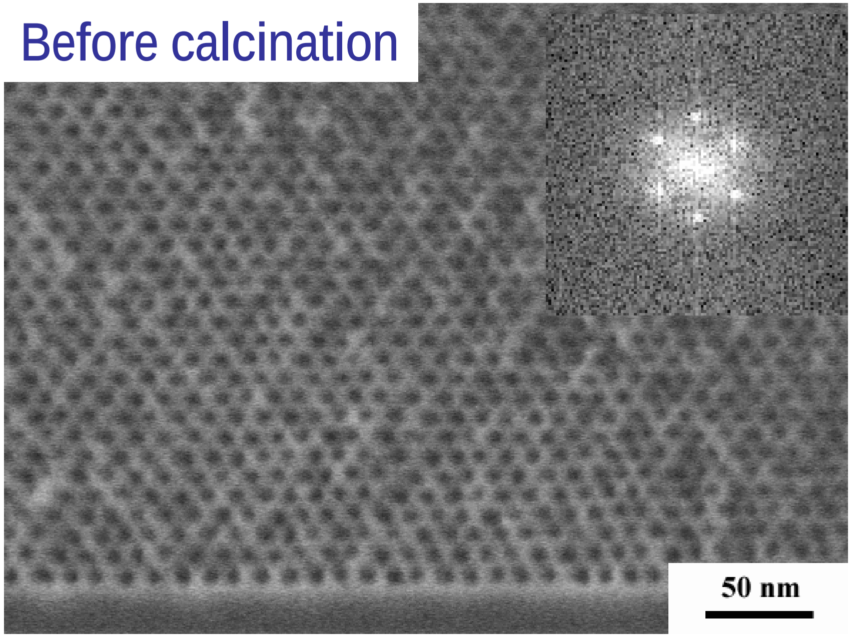
SEM and TEM images for the same mesostructure

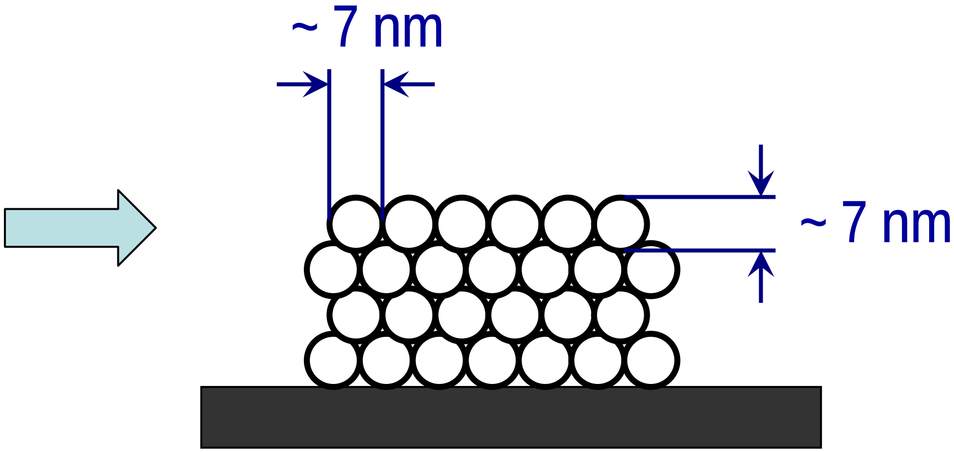


The TEM and SEM image of the same 2D hexagonal mesostructure were taken ((a) and (b), respectively) at the same position. The SEM image shows a solid picture of the sample and obviously present a clear mesostructure on the external surface of the sample, while the structure can not be observed by TEM.

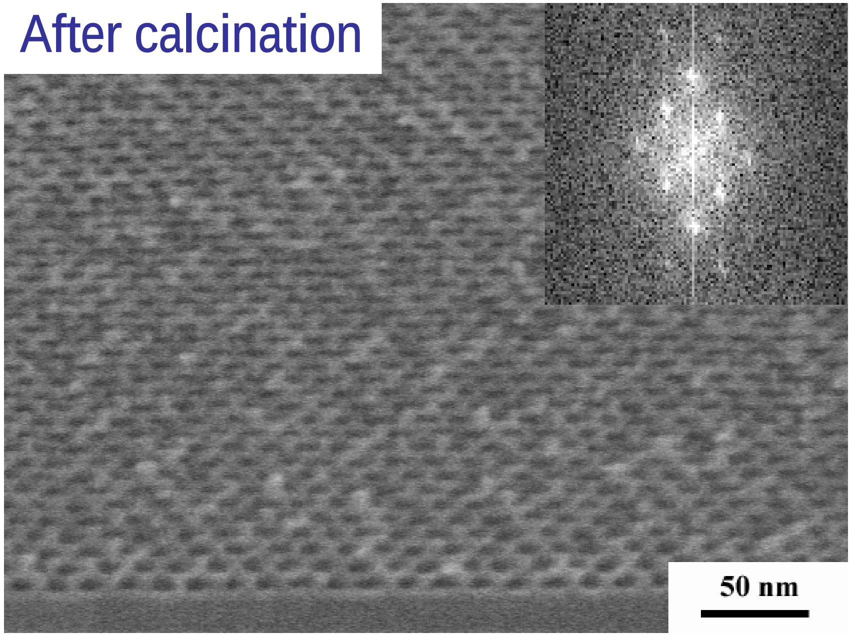
Results: Influence of Calcination on the Surface Morphology

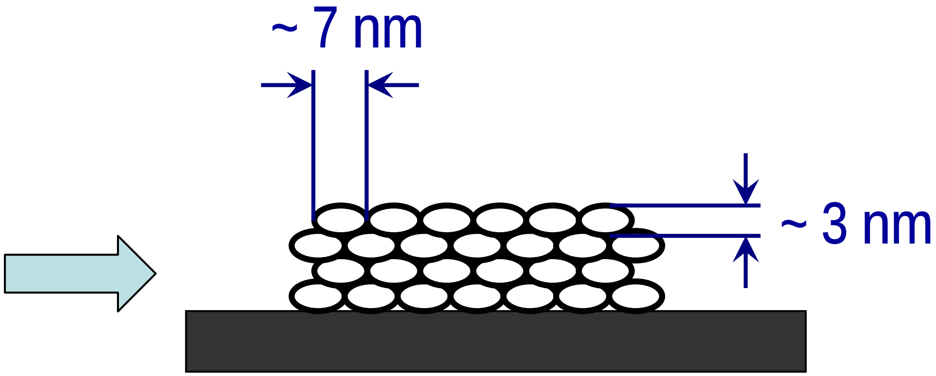
Before calcination





After calcination



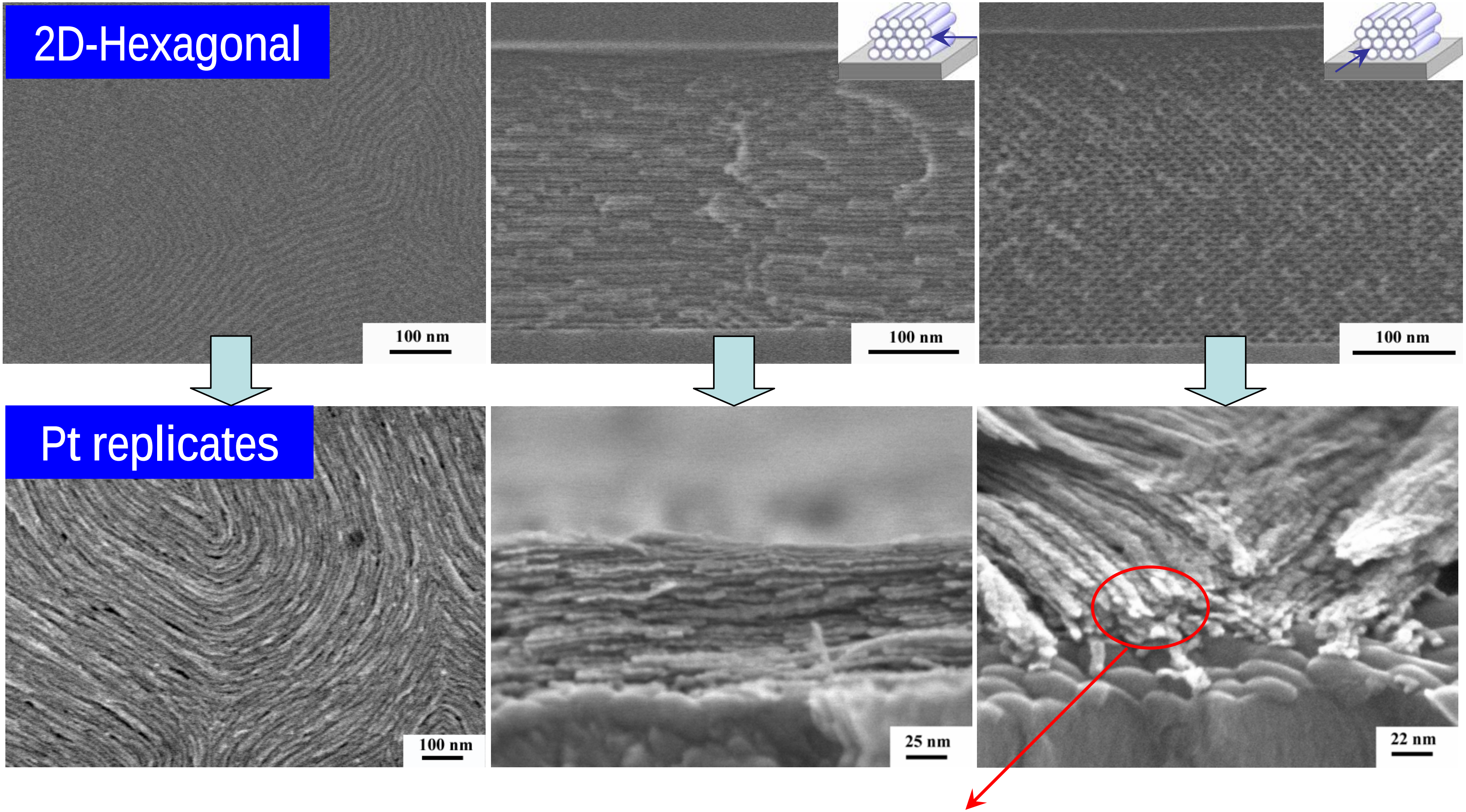


- Anisotropic contraction occurred in the direction perpendicular to the substrate upon calcination

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

Results: Pt Nanowire Thin Films Replicated from 2D hexagonal SiO_2 films

Top view | Cross-sectional view | Cross-sectional view



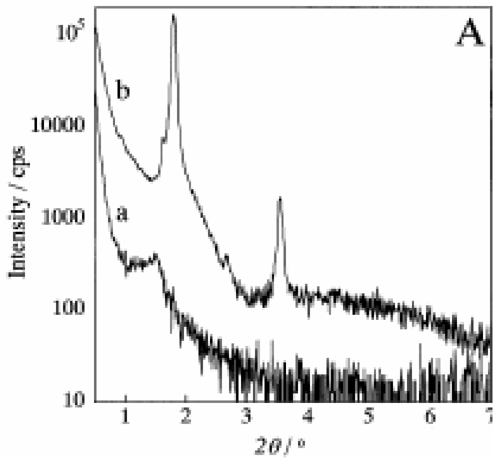
- Pt nanowires with ellipsoidal cross section

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

Mesostructured SnO_2 Film

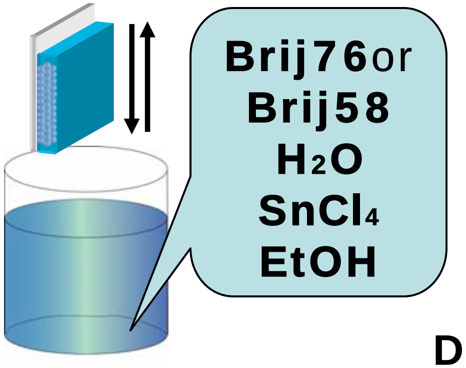
Mesostructured SnO_2 Film

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



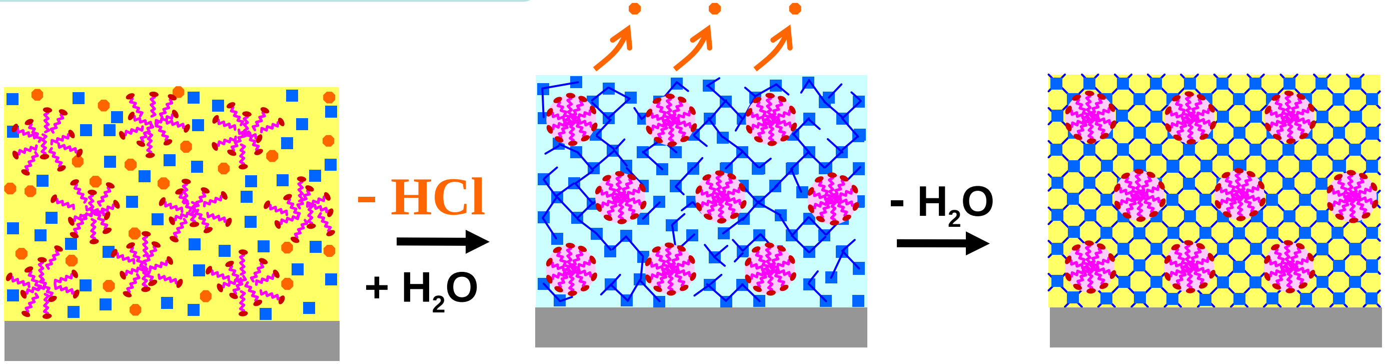
a: Without Water Vapor Treatment
b: After Water Vapor Treatment

Method


Brij76 or
Brij58
H_2O
$SnCl_4$
EtOH

Dip-Coating

Formation Process



Disordered Structure After Simple Drying

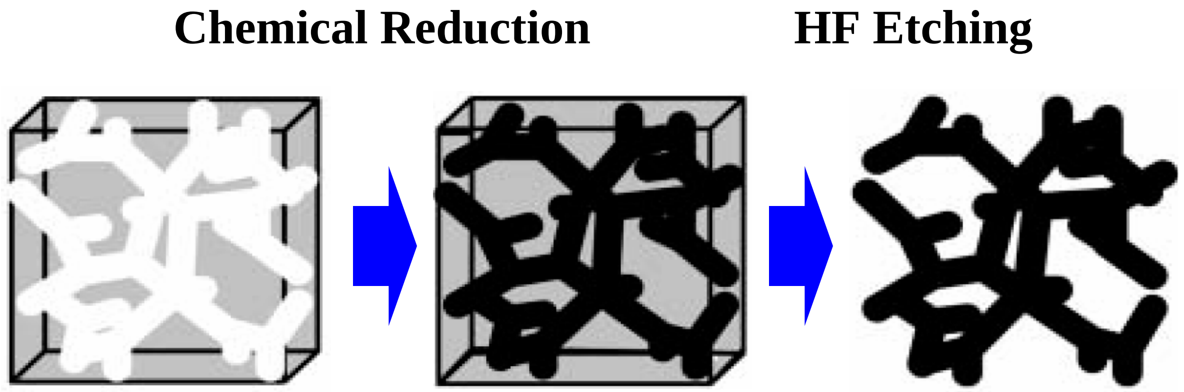
Water Vapor Treatment

Ordered Structure

Miyata, H., Noma, T. *Chem. Mater.*, **2003**, 15, 1334.

Synthesis Methods for Mesoporous Metals

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



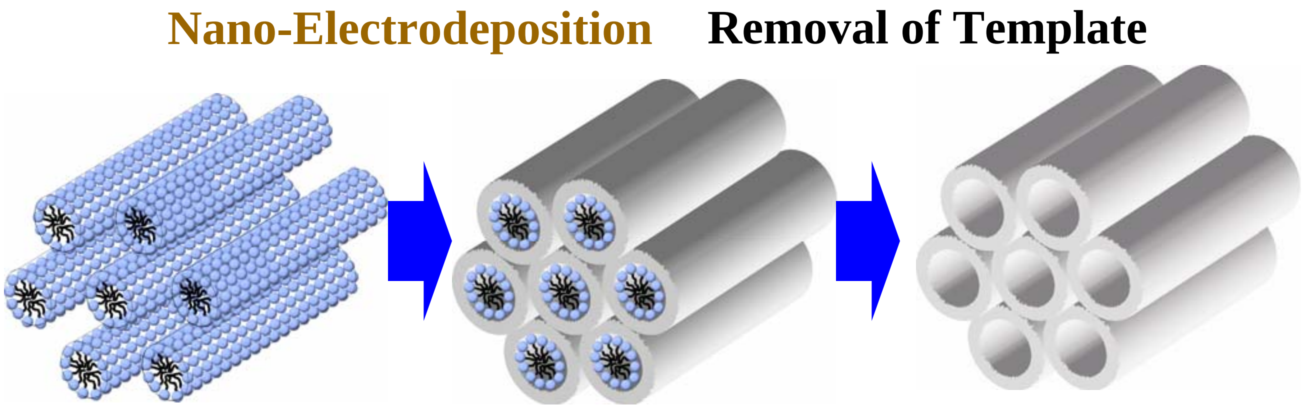
Chemical Reduction

HF Etching

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

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

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



Nano-Electrodeposition

Removal of Template

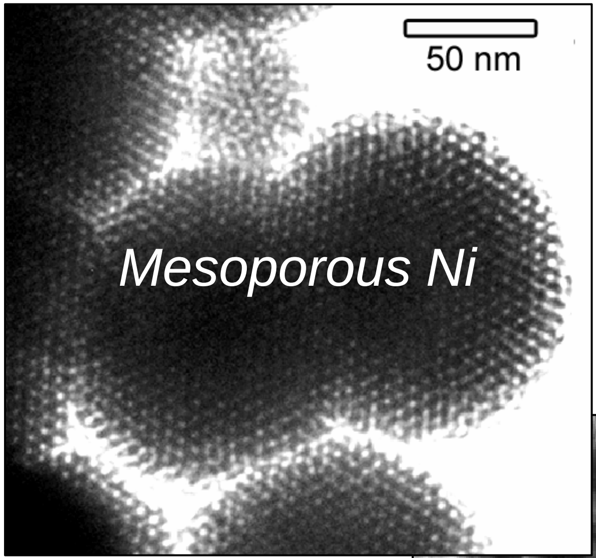
- **Soft-templates**
- **Various metals**
- **One-pot process**

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

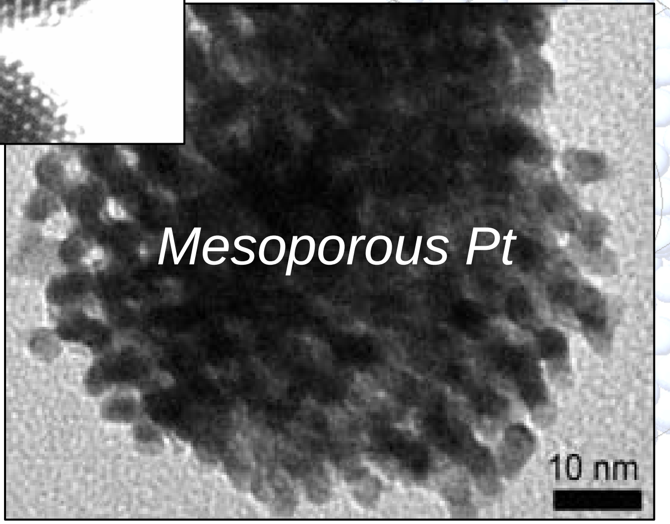
Our previous study

~Toward highly ordered mesoporous metals and alloys~

Finely controlled metallization

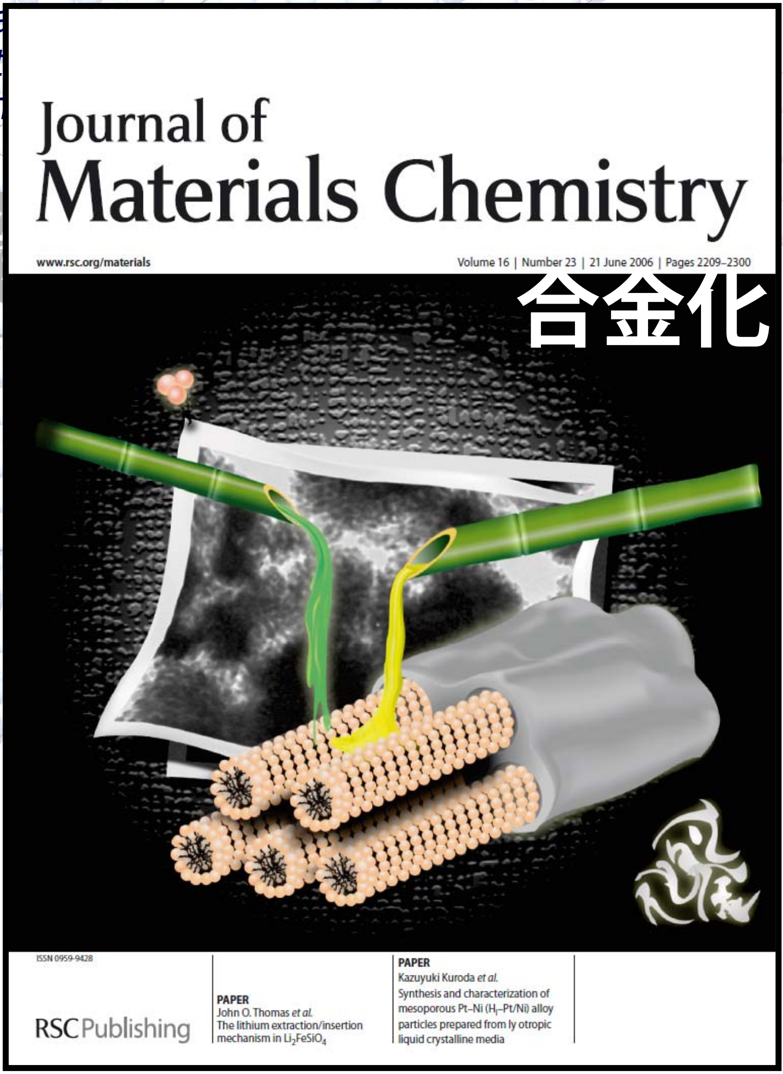


Y. Yamauchi *et al*., *Chem. Lett.*, **33**. 542 (2004).
Chem. Lett., **33**, 1576 (2004).
J. Ma
Elect
Chem



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).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Materials Chemistry
www.rsc.org/materials
Volume 16 | Number 23 | 21 June 2006 | Pages 2209–2300

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ISSN 0959-9428
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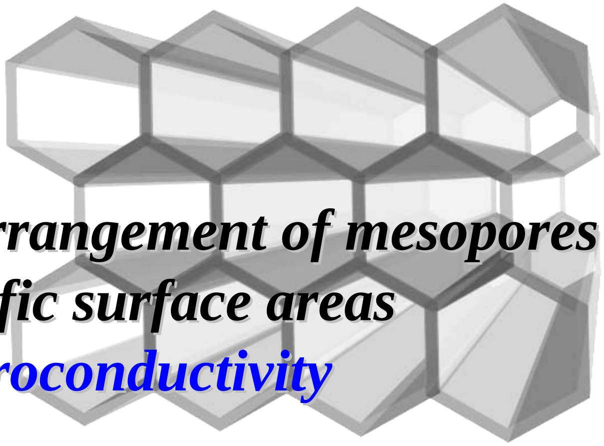
John O. Thomas *et al.*
The lithium extraction/insertion mechanism in Li_2FeSiO_4

PAPER
Kazuyuki Kuroda *et al.*
Synthesis and characterization of mesoporous Pt–Ni (H_1–Pt/Ni) alloy particles prepared from lyotropic liquid crystalline media

Mesoporous Metals toward Nanostructured Catalysts



Periodic arrangement of mesopores
High specific surface areas
High electroconductivity

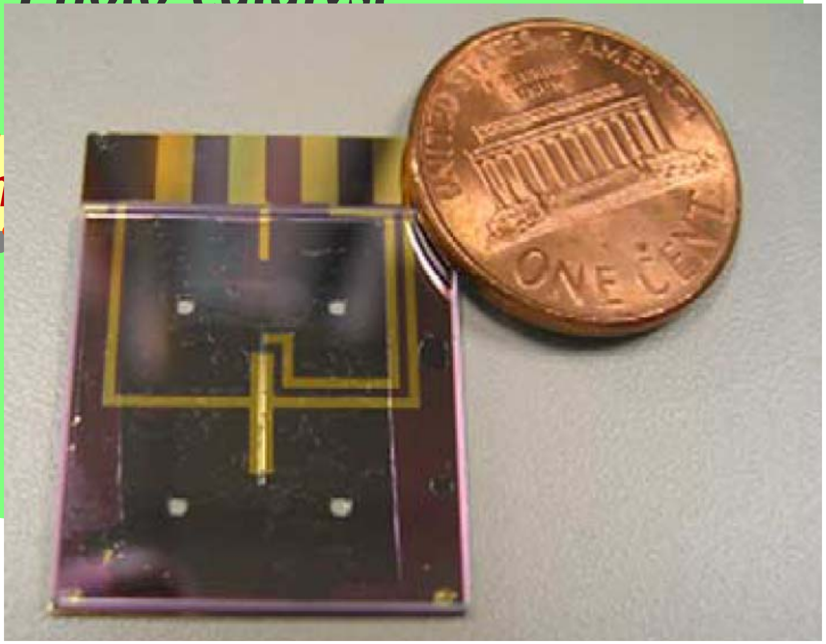
Synthesis

Highly ordered mesostructure
Structural resolution
Alloying in pore wall

Environmental Catalysts

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

En



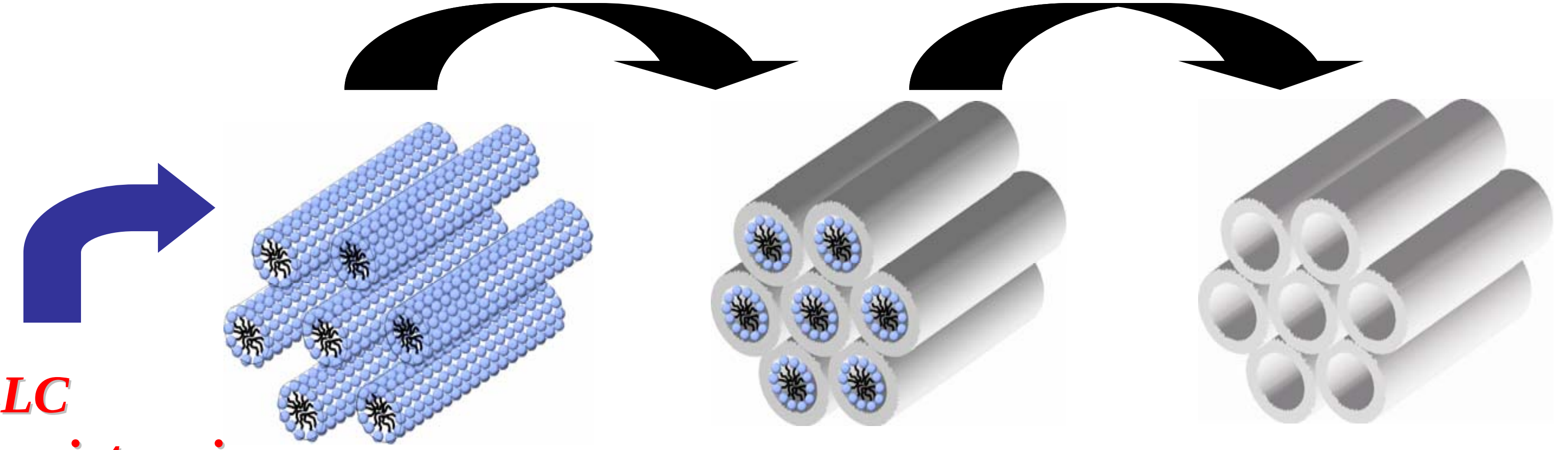
Development of New Approach for Microfabrication

Novel Applications Micro-sensors, Micro-batteries, Micro-bioactive materials, Miniaturized devices, etc…

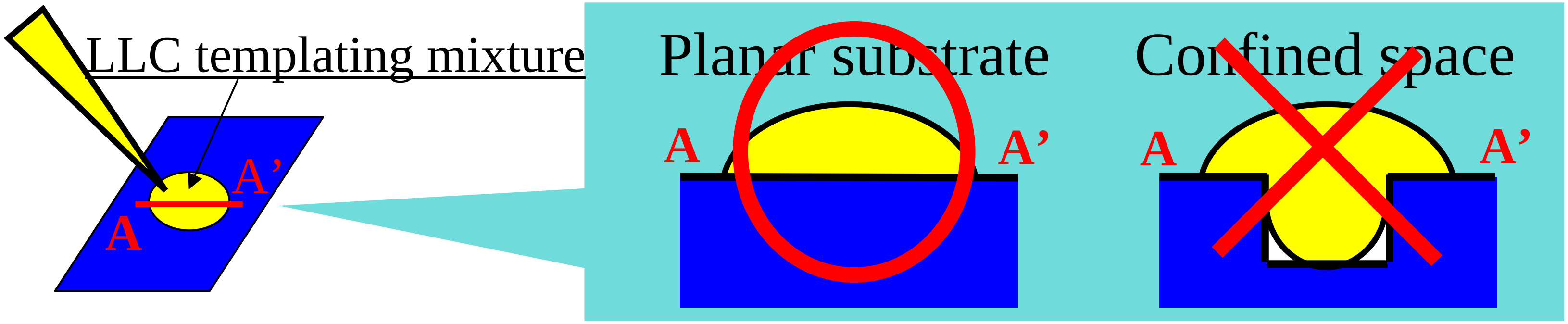
Microfabrication of Mesoporous Metals

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

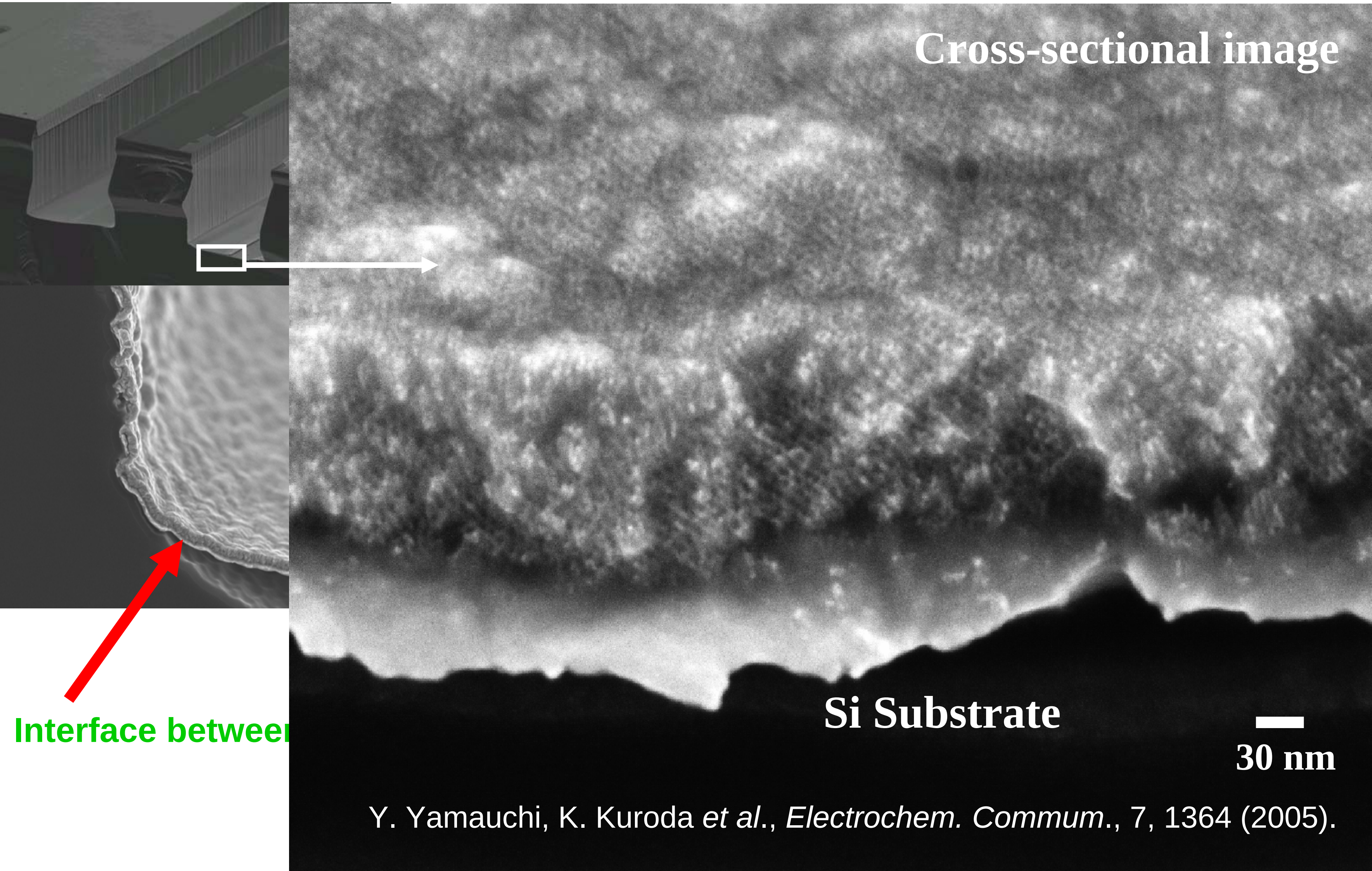
Novel Applications micro-sensors, micro-batteries, micro-bioactive materials, miniaturized devices, etc…



General LLC templating mixture is <u>highly viscous!</u>



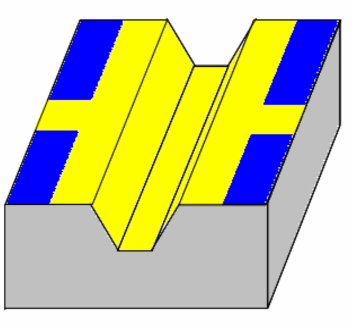
Bottom Surface in Microchannel

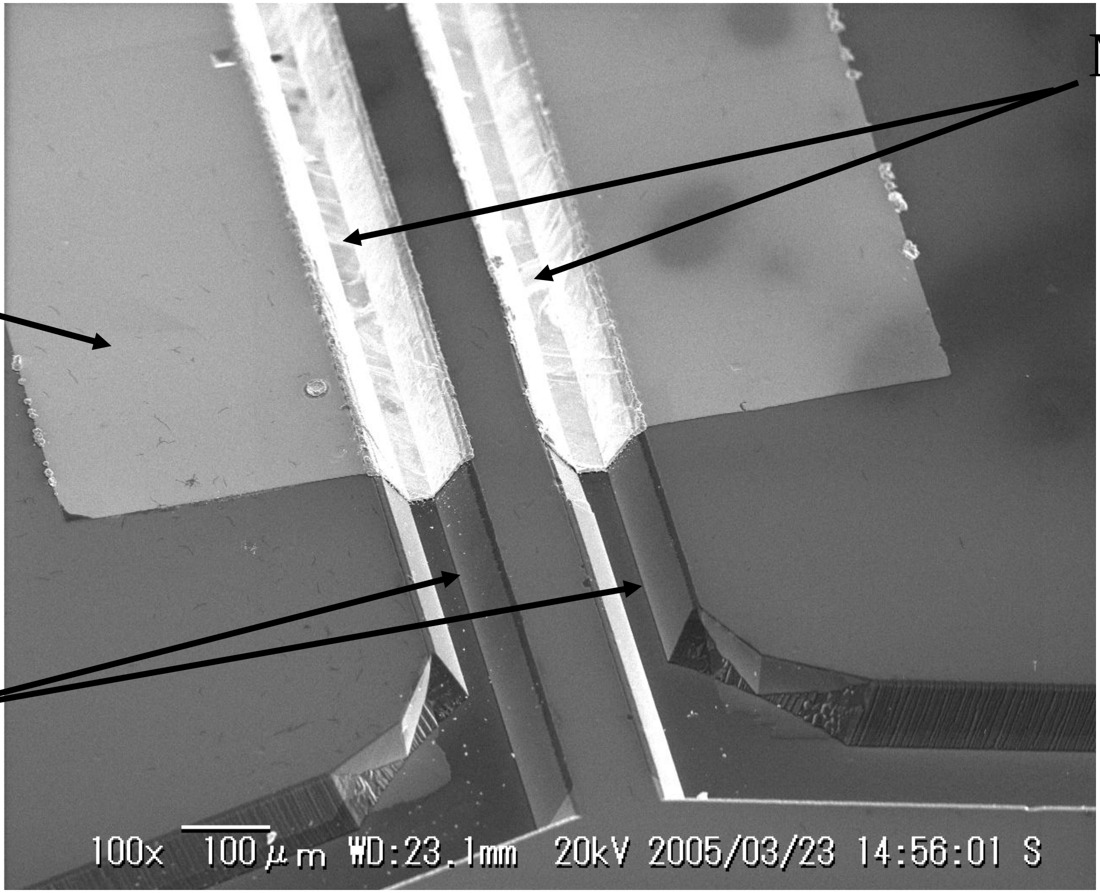


Interface betwee

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

SEM Observation





Mesoporous Pt

Au/Ti/SiO_2

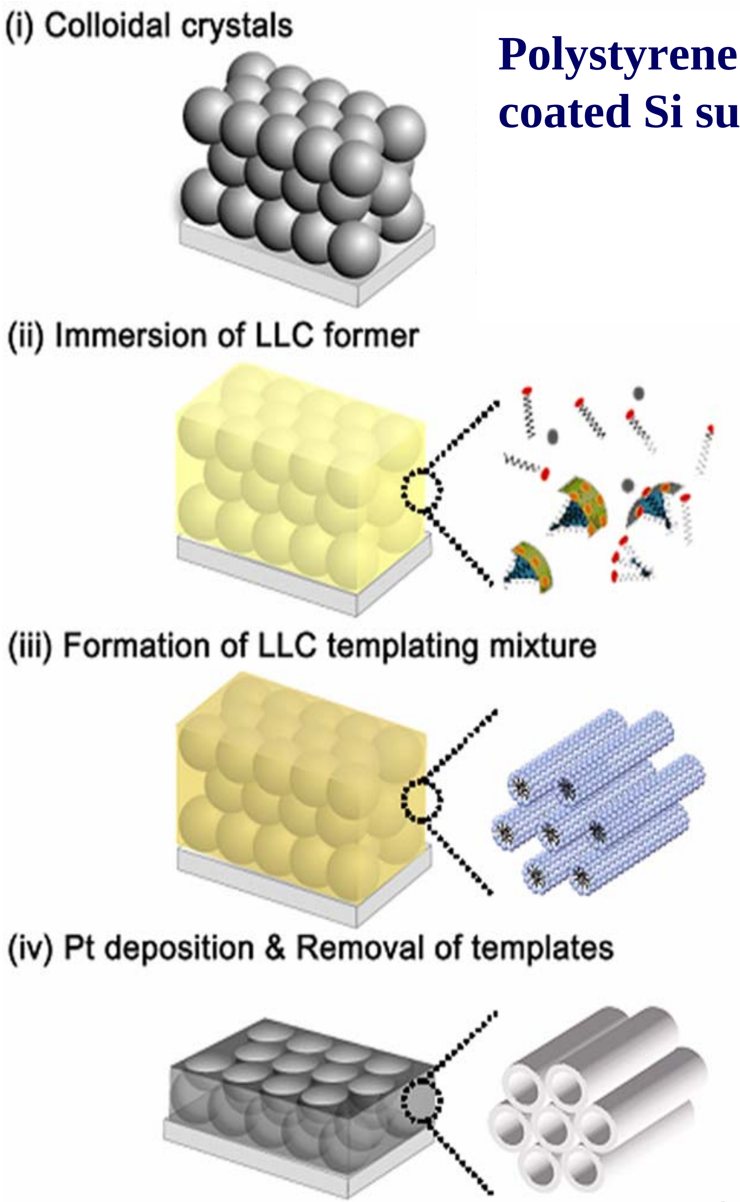
Microchannels

Successful deposition of mesoporous Pt only inside microchannels

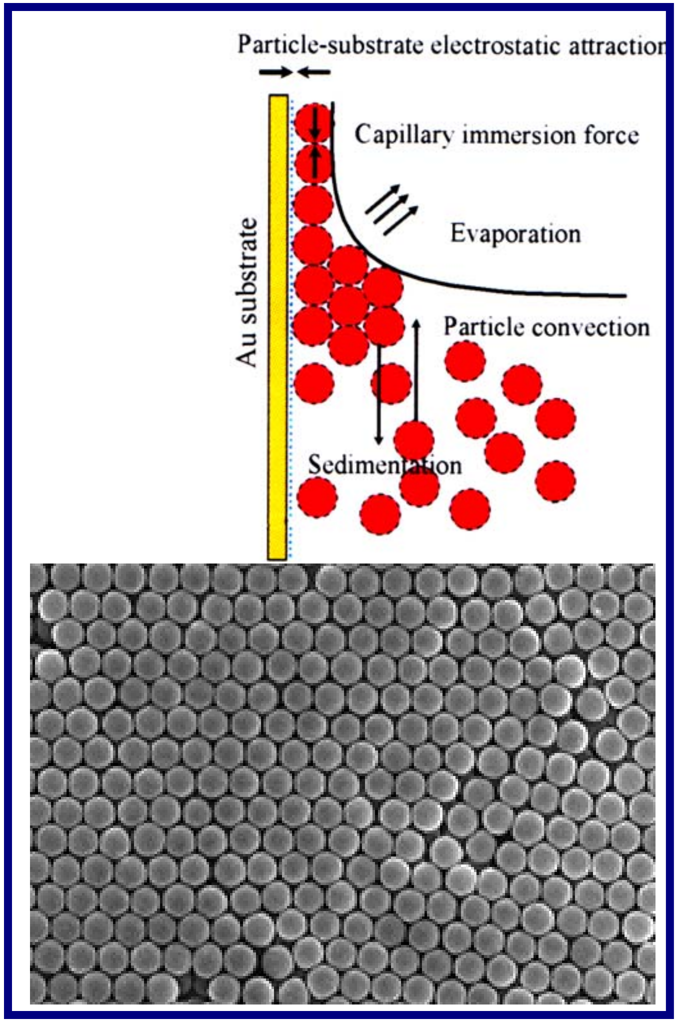
Y. Yamauchi *et al*., *Electrochem. Commum*., 7, 1364-1370 (2005).

Experimental procedure for Hierarchical porous electrode

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

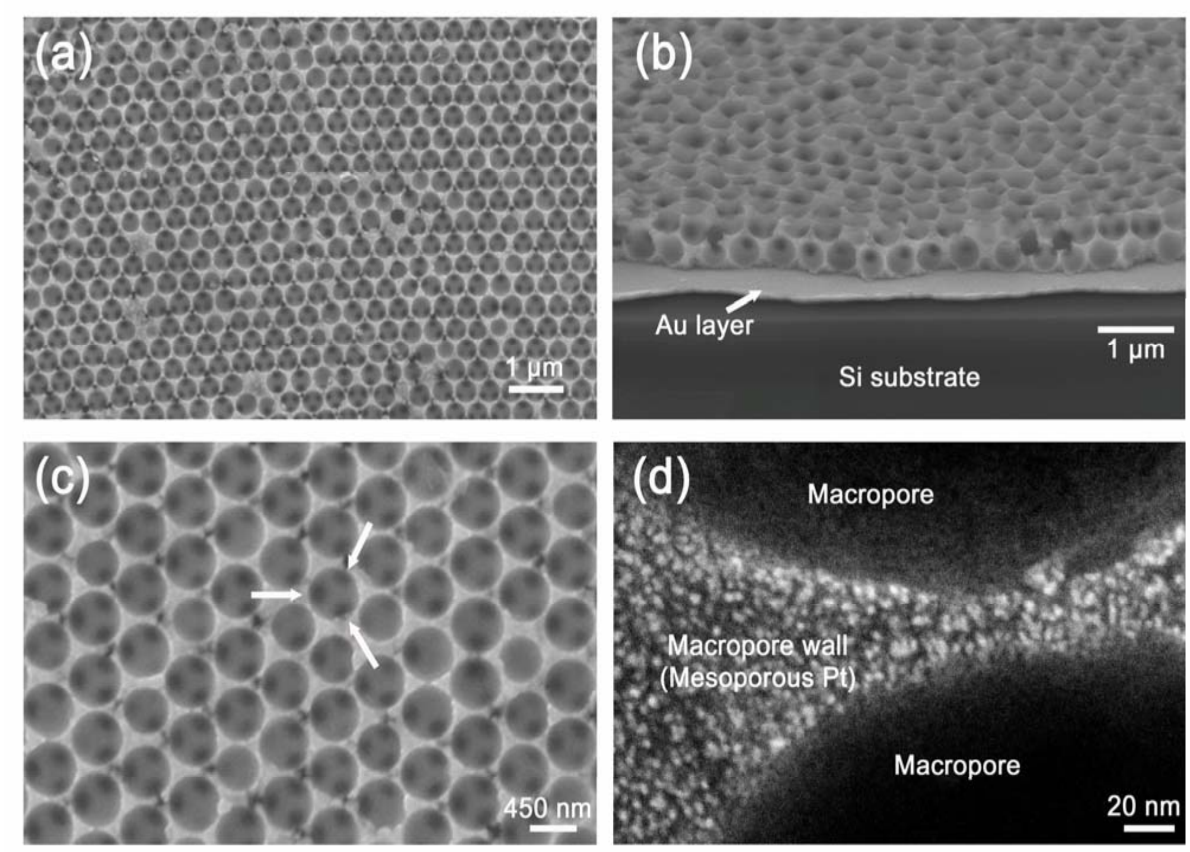


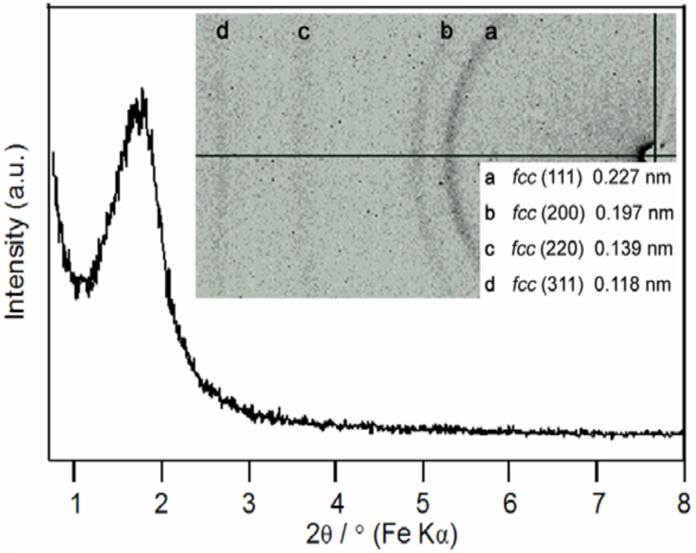
$C_{16}(EO)_8$
H_2PtCl_6
H_2O
C_2H_5OH



Y. Yamauchi and K. Kuroda, *Electrochem. Commum.*, in press (2006).

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.

Y. Yamauchi and K. Kuroda, *Electrochem. Commum*., in press (2006).

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”

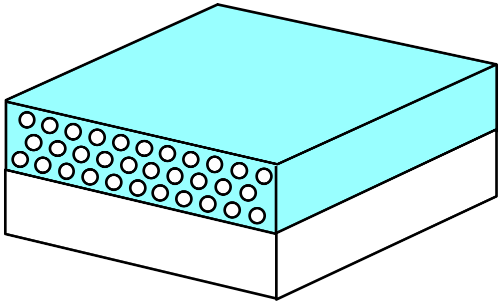
- **Perpendicular Orientation**

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.

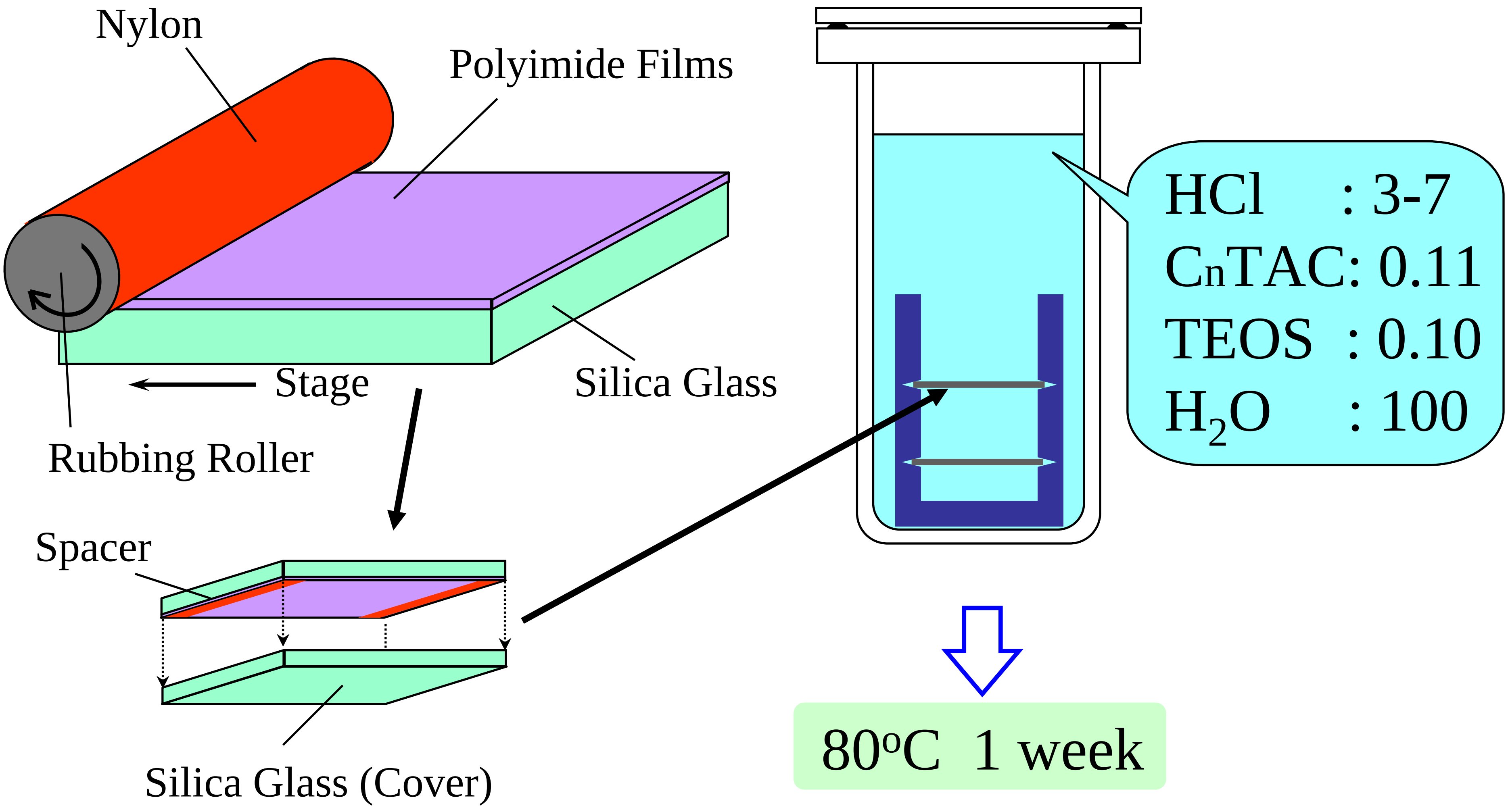
e) Miyata, H., Kuroda, K. *Chem. Mater.* **1999**, 11, 1609.
Miyata, H., Kuroda, K. *Chem. Mater.* **2000**, 12, 49.
Miyata, H., Kuroda, K. *Chem. Mater.* **2002**, 14, 766.

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

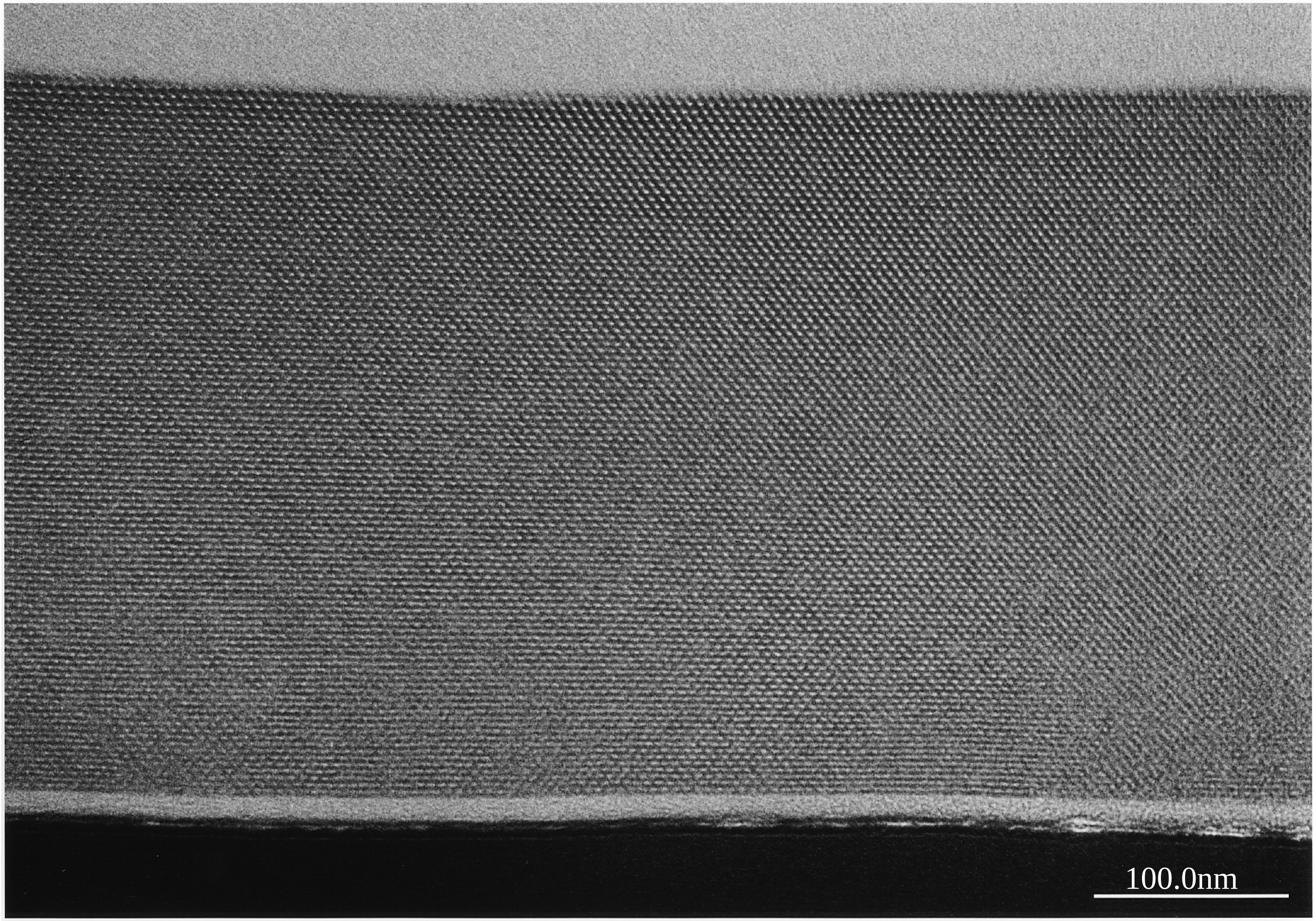


HCl : 3-7
C_nTAC: 0.11
TEOS : 0.10
H_2O : 100

80°C 1 week

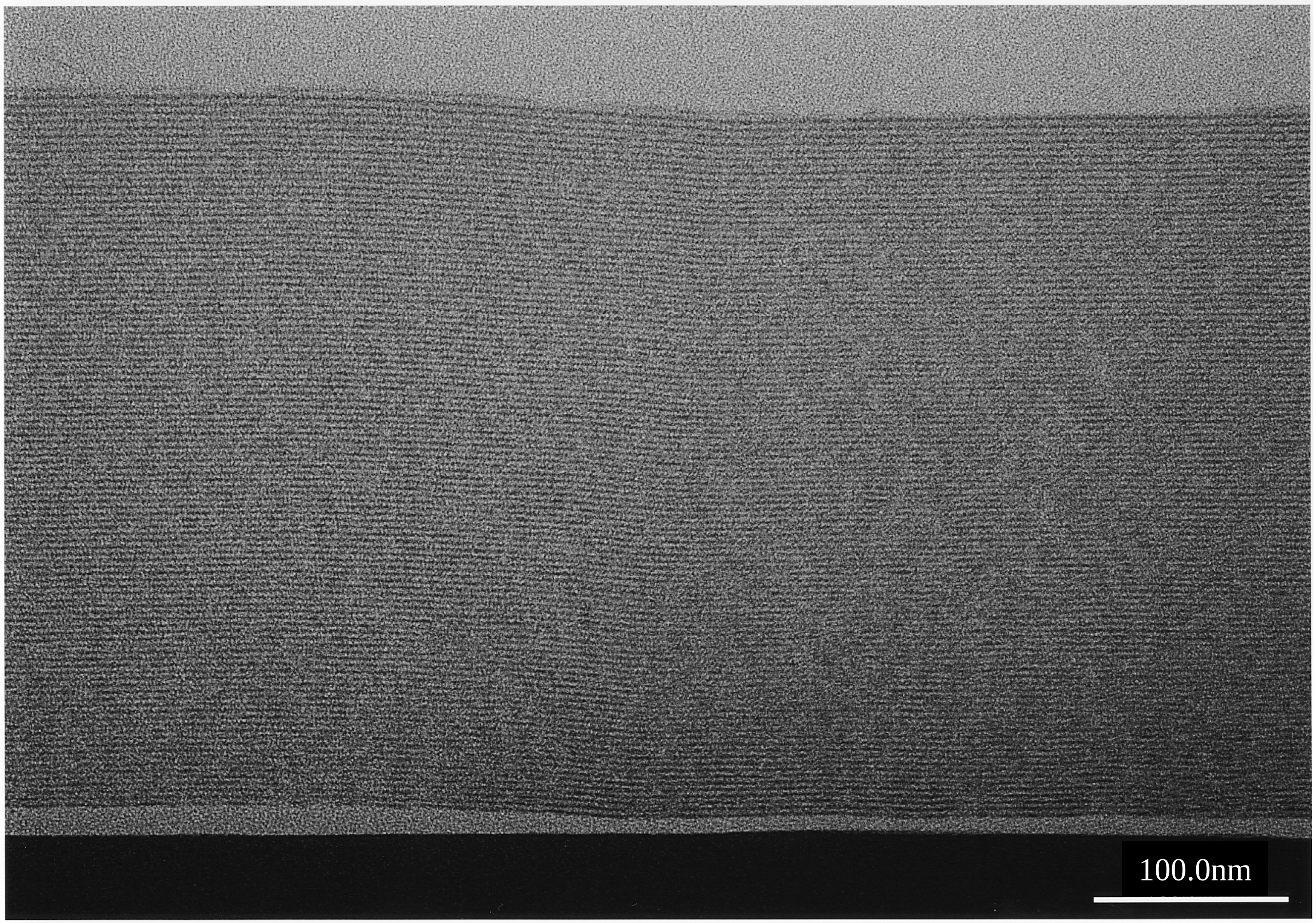
Cross-sectional TEM of the MPS on the PI-2 Film

Sliced Parallel to the Rubbing Direction



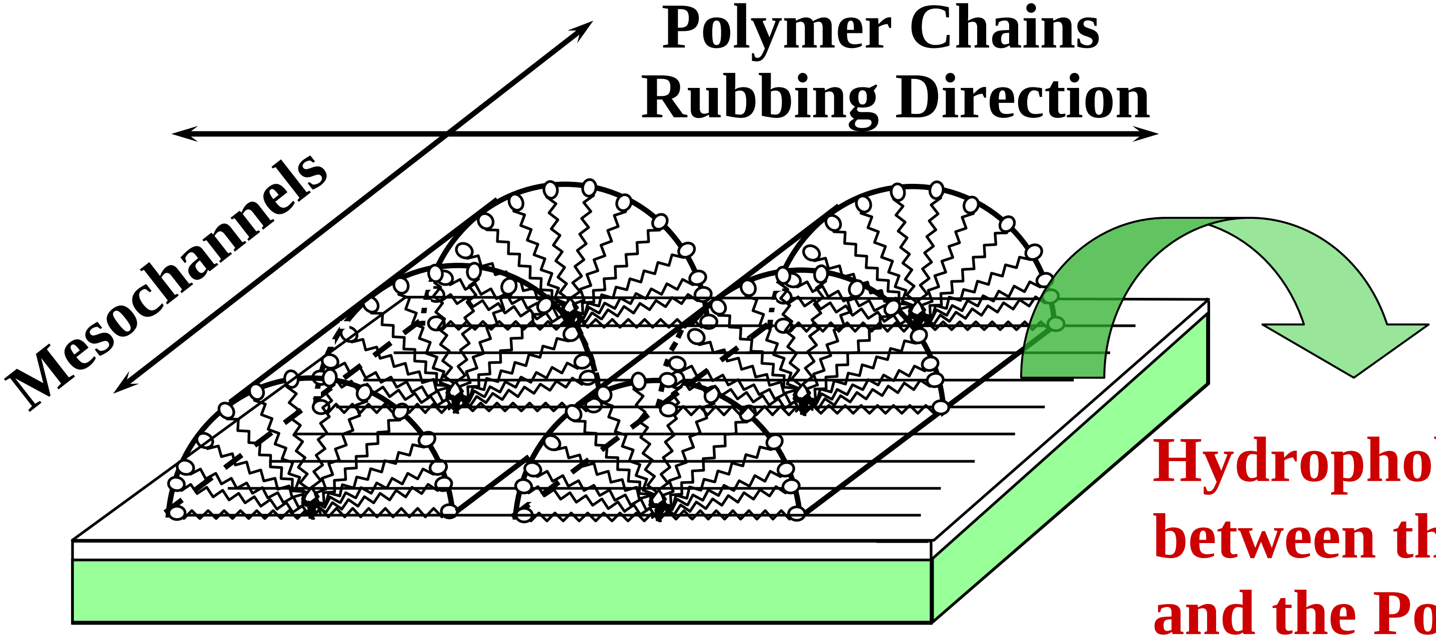
Cross-sectional TEM of the MPS on the PI-2 Film

Sliced Normal to the Rubbing Direction



Alignment Mechanism

Alignment Model on the Rubbing-treated PI-2 Film



Polymer Chains
Rubbing Direction

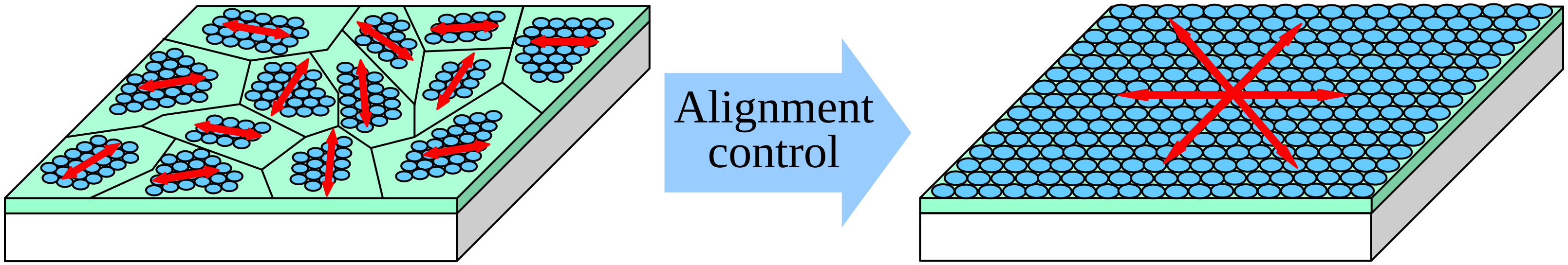
Mesochannels

Hydrophobic Interactions
between the Surfactant
and the Polymer Chains

Requirements for the Polymer

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

Single crystalline porous structure of mesoporous silica films

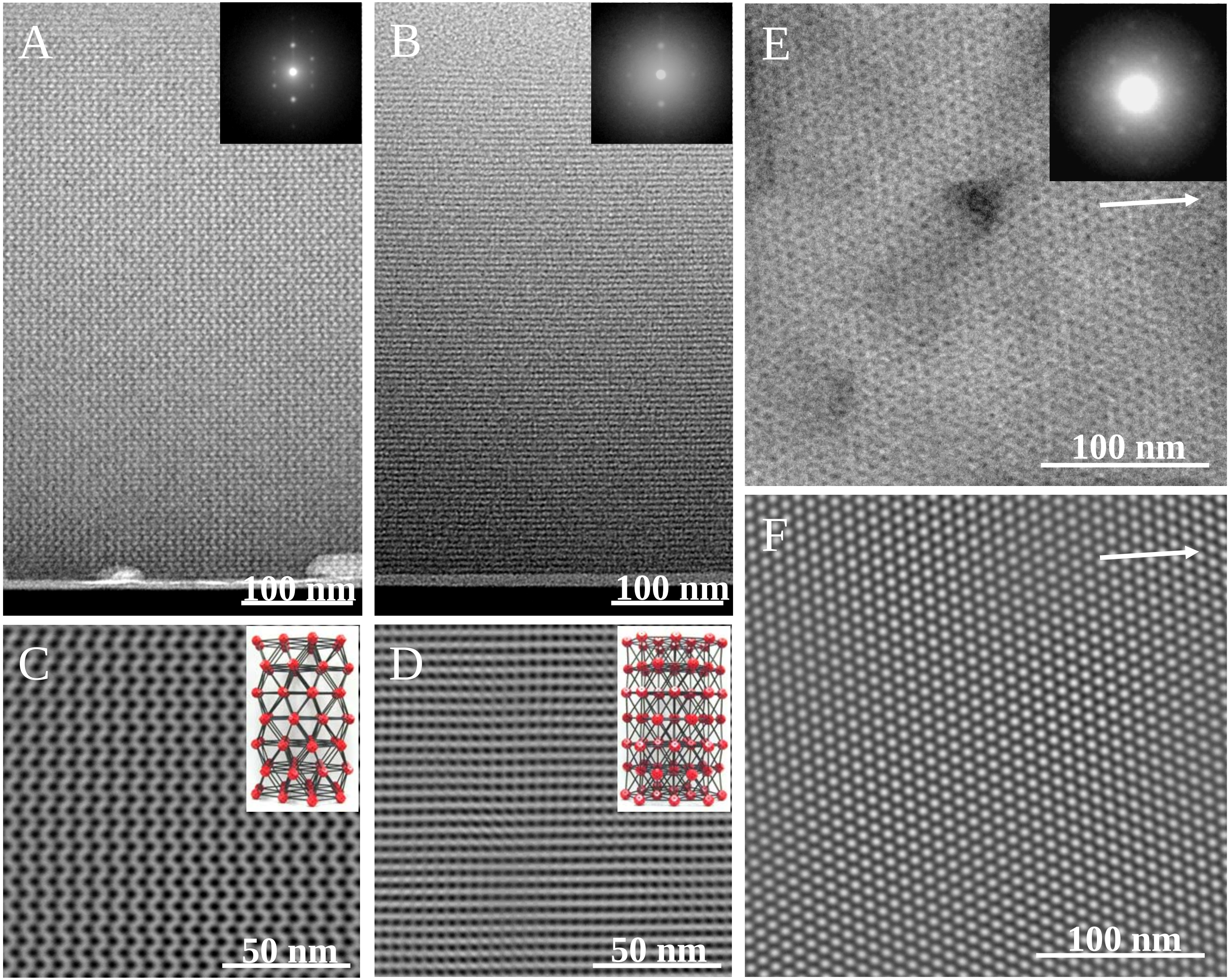


Polycrystalline porous structure

Single crystalline porous structure

H. Miyata et al., *Nat. Mater.*, 3, 651(2004)

Scheme 1



Nat. Mater. (2004)

Figure 1

Variation of the porous structure

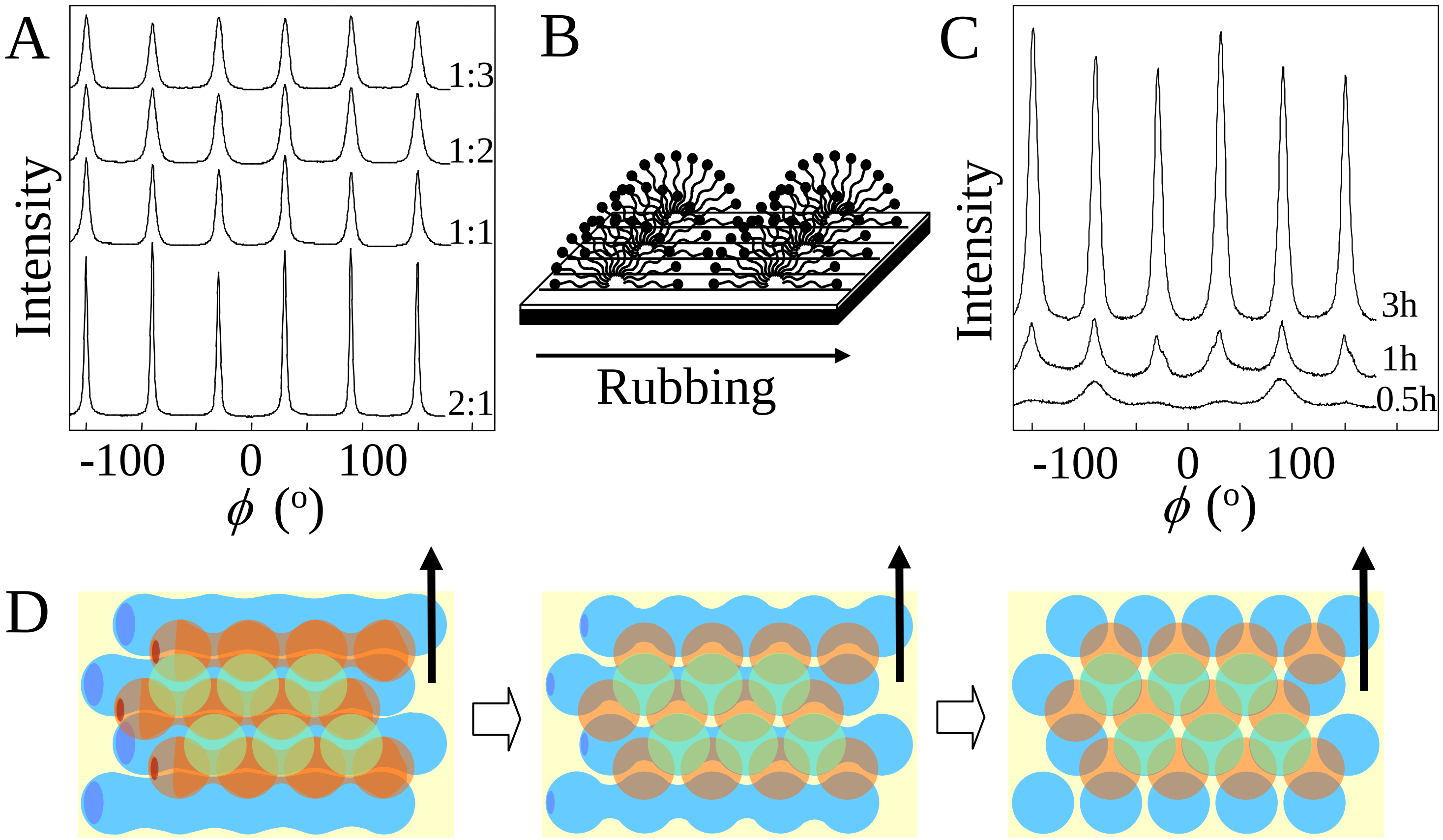


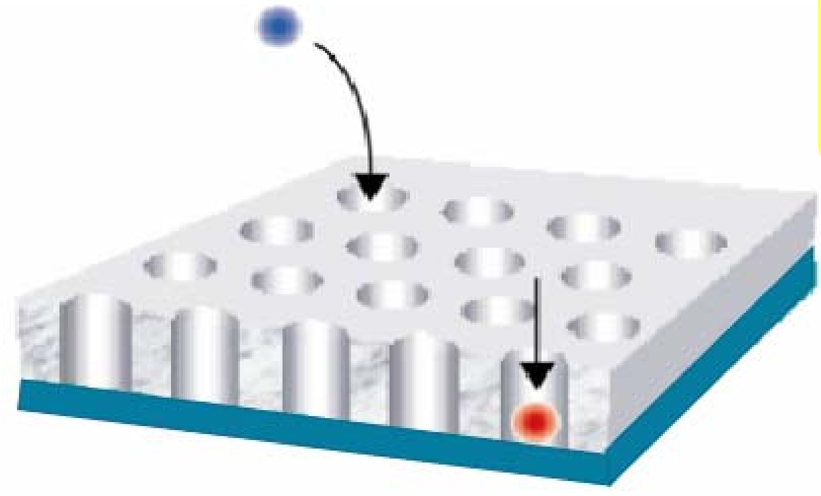
Figure 3

Nat. Mater. (2004)

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

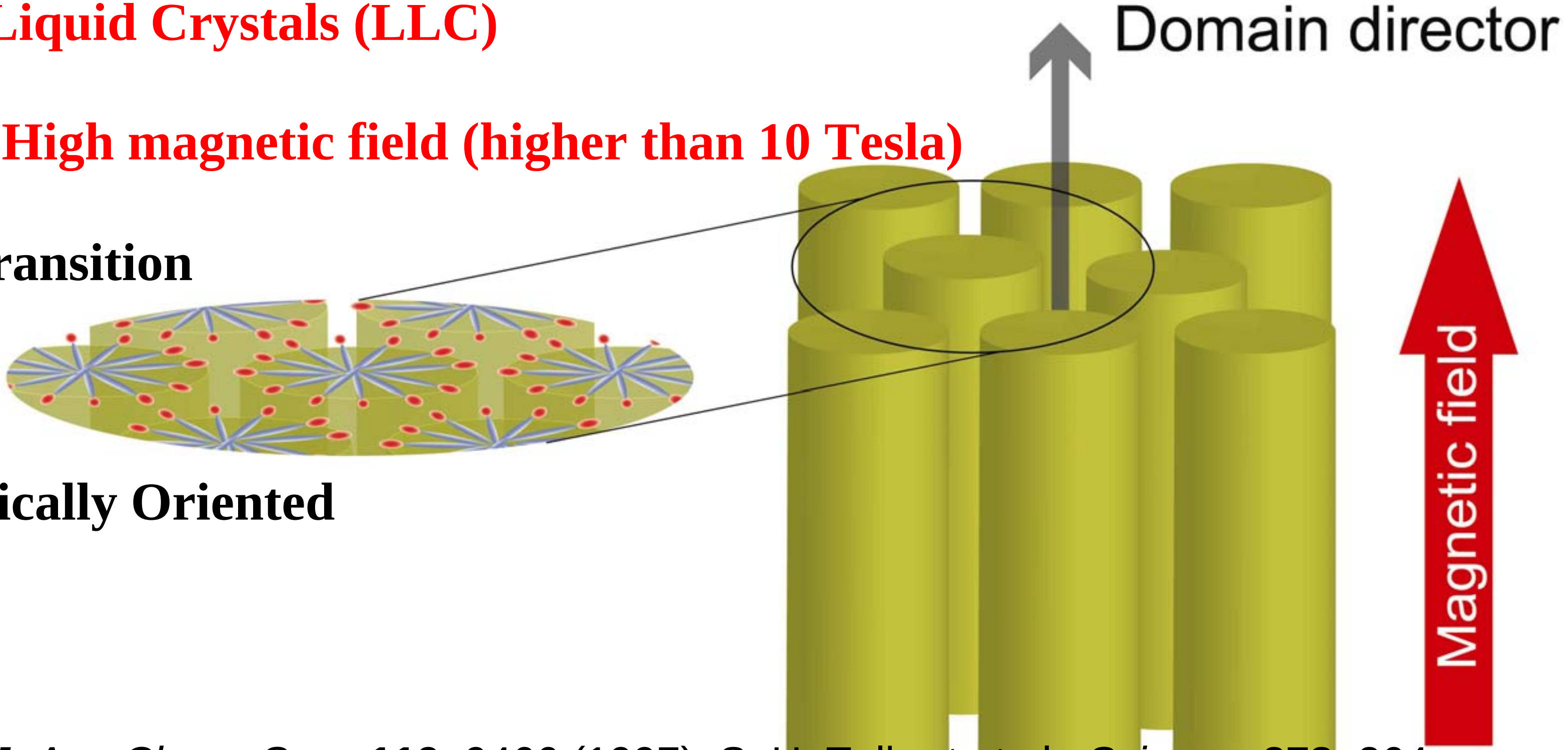
Surfactant (diamagnetic substance)

Lyotropic Liquid Crystals (LLC)

High magnetic field (higher than 10 Tesla)

Magnetic transition

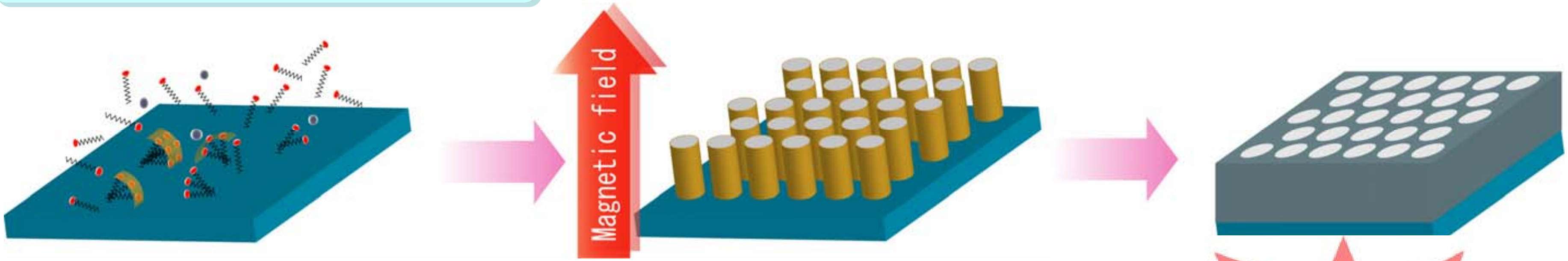
Macroscopically Oriented Mesophase

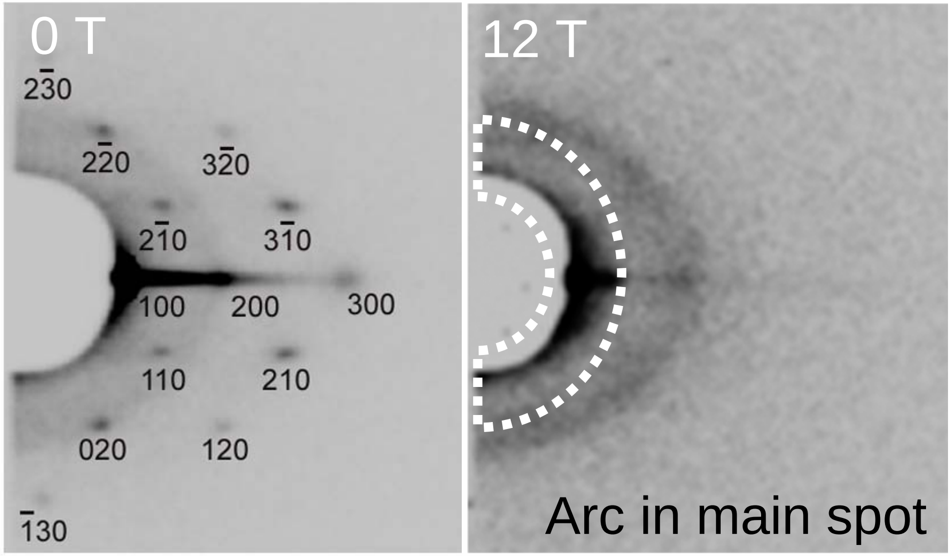


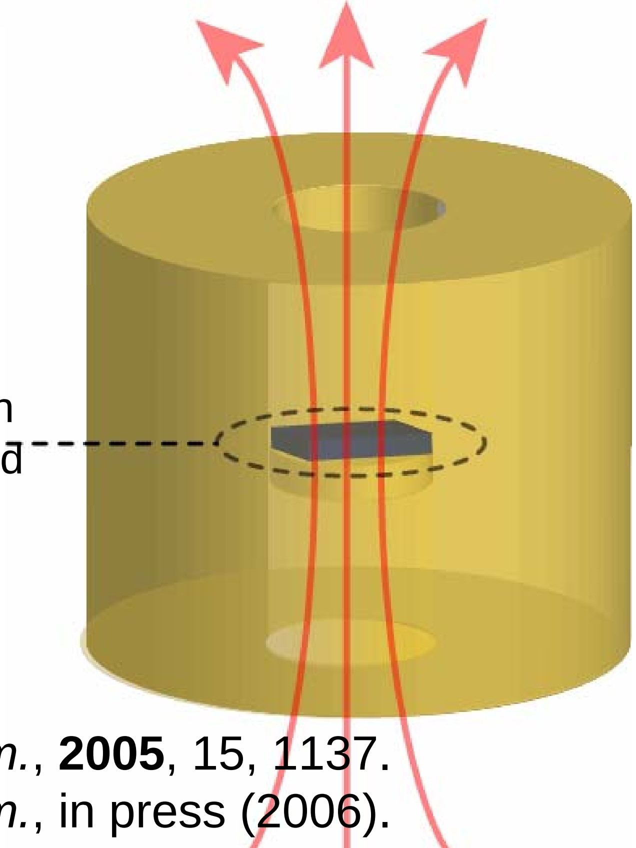
A. Firouzi *et al.*, *J. Am. Chem. Soc.*, **119**, 9466 (1997); S. H. Tolbert et al., *Science*, **278**, 264 (1997); T. Grigorova *et al.*, *Macromolecules*, **38**, 7430 (2005); A. Rapp *et al.*, *J. Phys. Chem. B,* **103**, 1705 (1999); M. Ogura *et al.*, 4th International Mesostructured Materials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

Magnetically induced orientation of mesochannels in mesoporous silica films

Formation Process





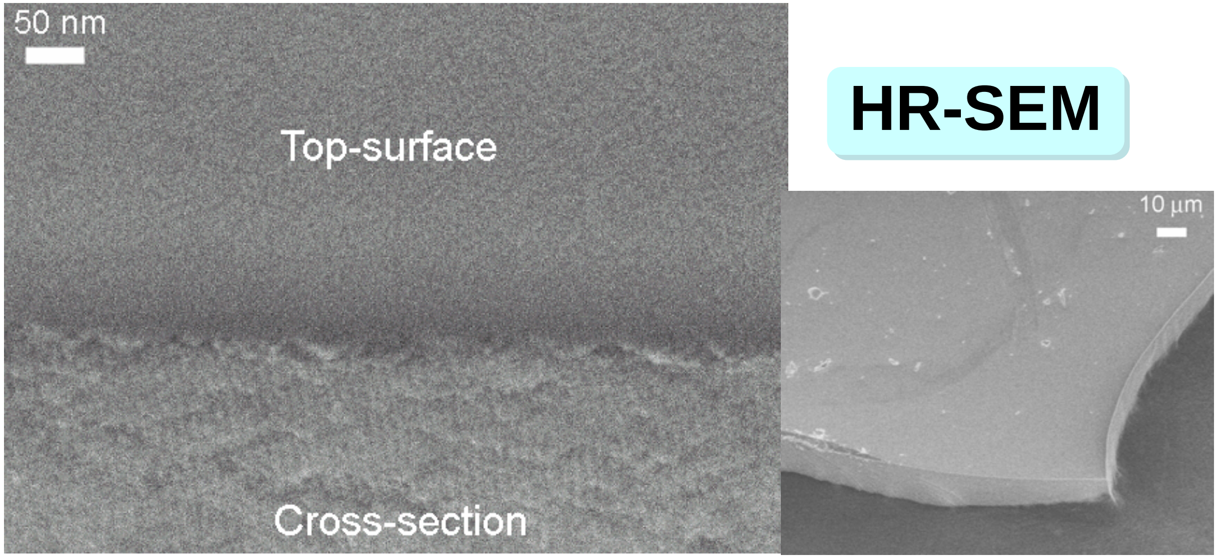


Under a high magnetic field (12 Tesla)

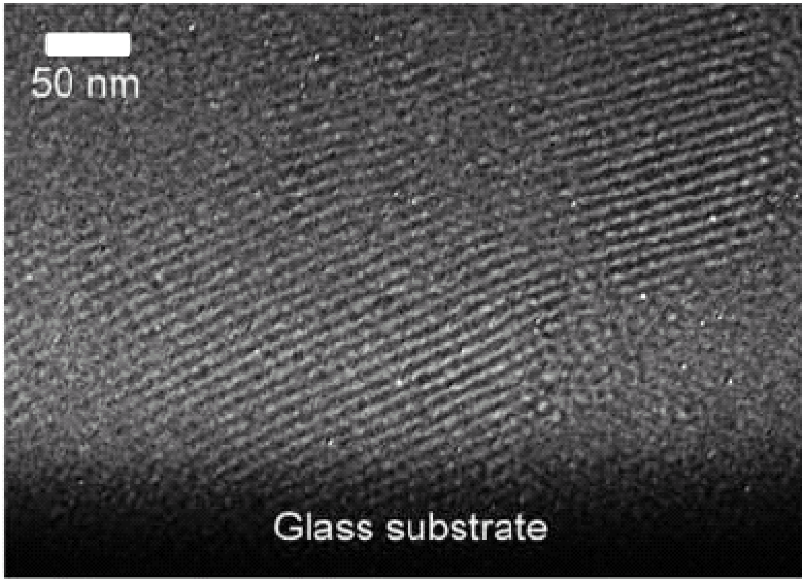
Y. Yamauchi, M. Sawada, K. Kuroda *et al*., *J. Mater. Chem.*, **2005**, 15, 1137.
Y. Yamauchi, M. Sawada, K. Kuroda *et al*., *J. Mater. Chem.*, in press (2006).

Magnetically induced Orientation

HR-SEM

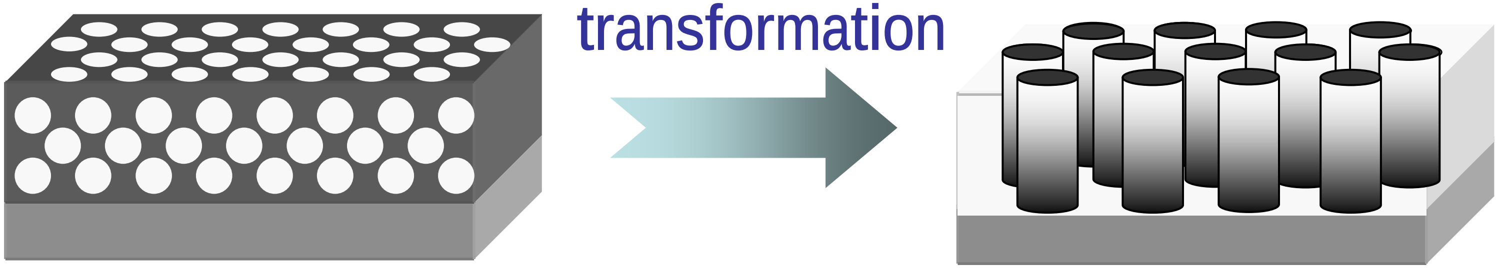


TEM



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

Synthesis of crystalline mesoporous TiO_2 thin films with a vertical porosity



Structural transformation

3D hexagonal structure

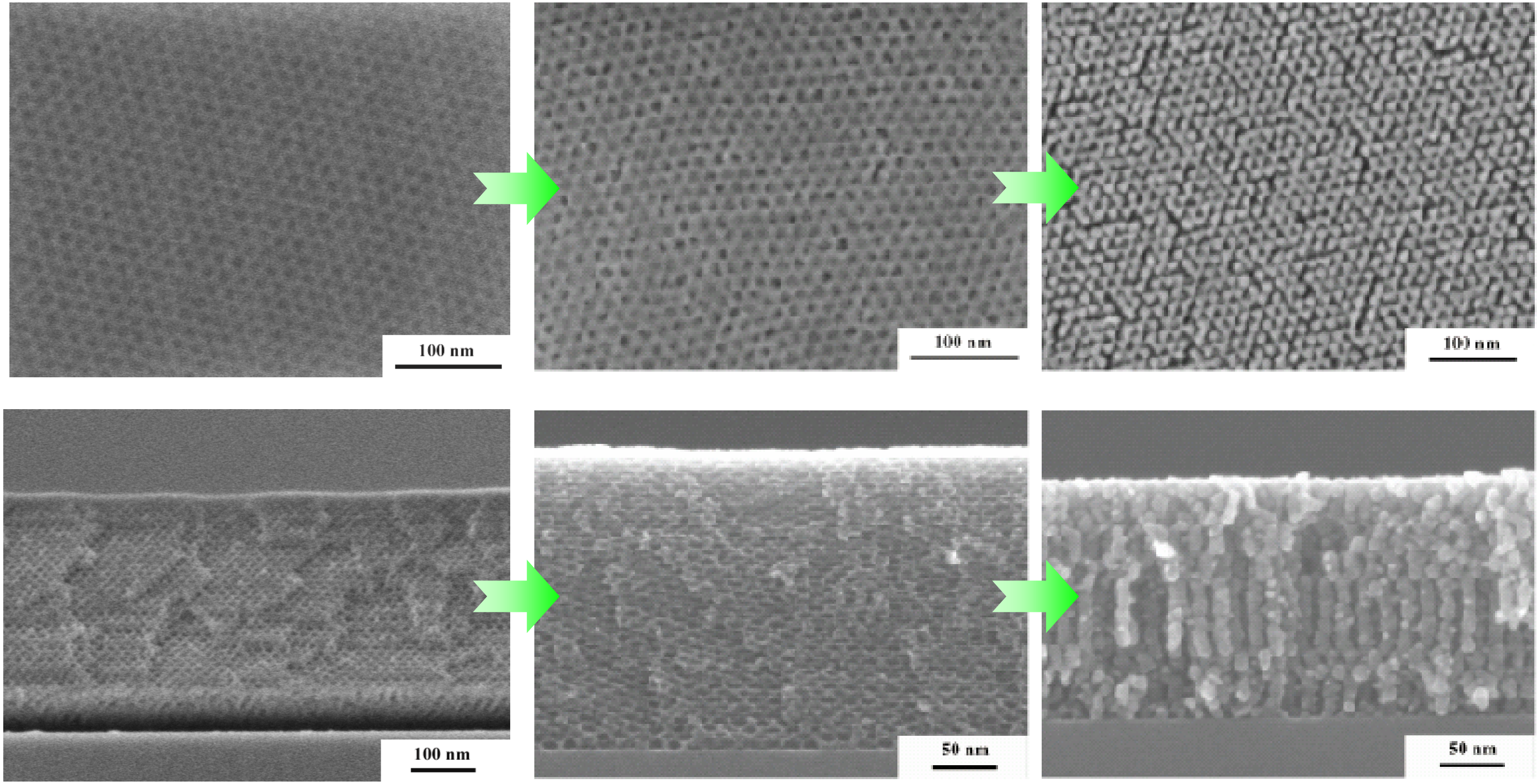
Nanopillar thin film with vertical porosity

- Appropriate reactant ratios
- Low aging temperatures

- Crystallline pillars
- A vertical and continuous porosity

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

Results: FE-SEM Observation



As-synthesized

200°C

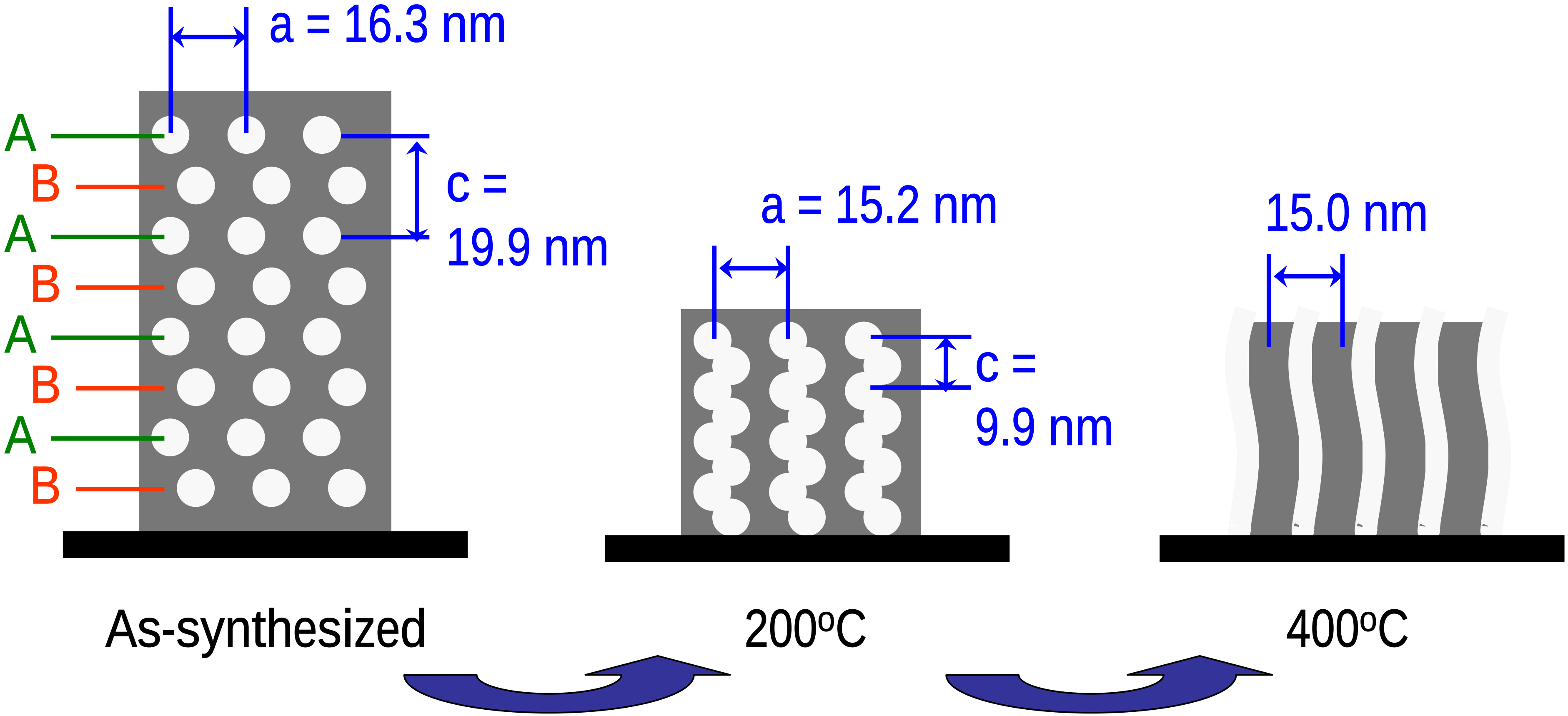
400°C

3D hexagonal mesoporous structure

TiO_2 nanopillar arrays with vertical porosity

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

Discussion: Formation Mechanism of TiO_2 Pillars – Cross Section

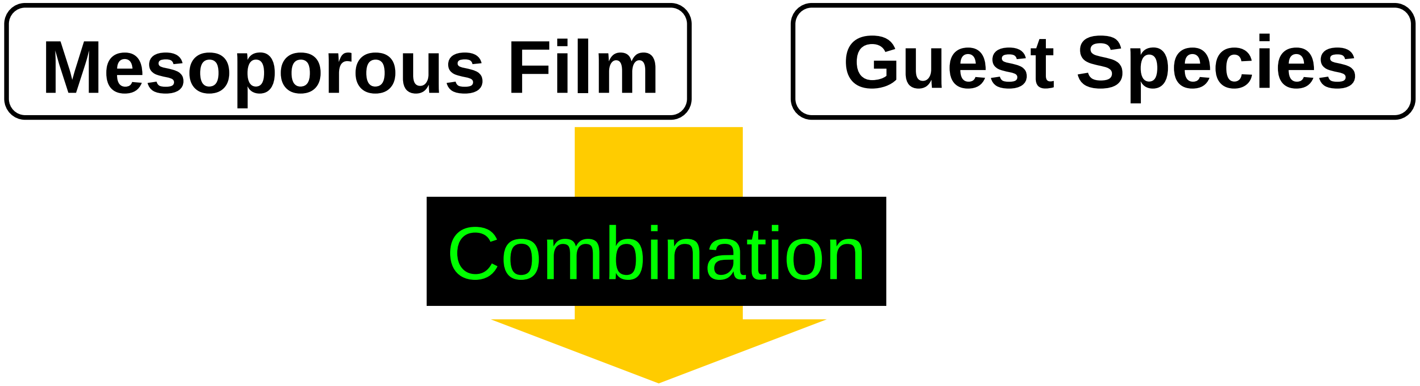


A large contraction in the direction vertical to the substrate

Crystallization of TiO_2 framework upon calcination

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

Incorporation of Various Guest Species



Mesoporous Film

Guest Species

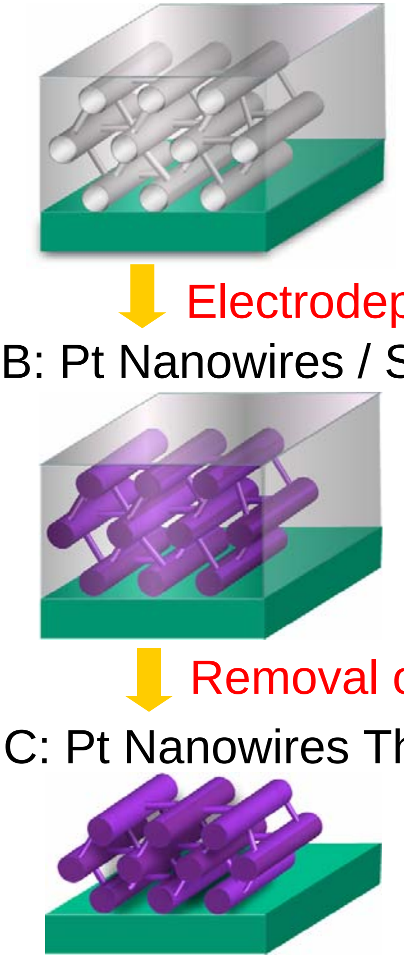
Combination

■ **Control of Orientation, Conformation and Interactions**

Guest Species

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

Well-aligned Pt Nanowires (1)



A: Mesoporous Silica Film

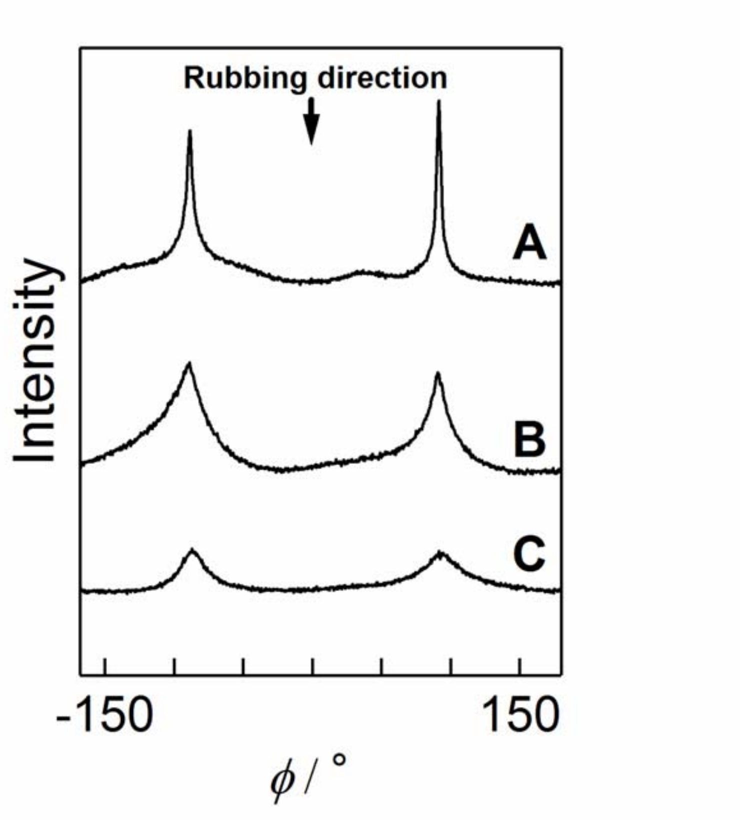
Electrodeposition

B: Pt Nanowires / Silica

Removal of Silica Template

C: Pt Nanowires Thin Film

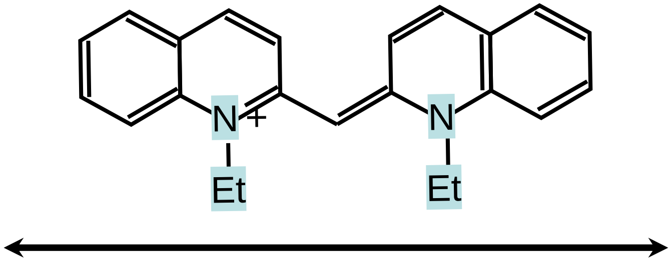
In-plane XRD



Suzuki, Kuroda, K. IMMS2006, P-128

Incorporation of Dye (Cyanine Dye)

Cyanine Dye



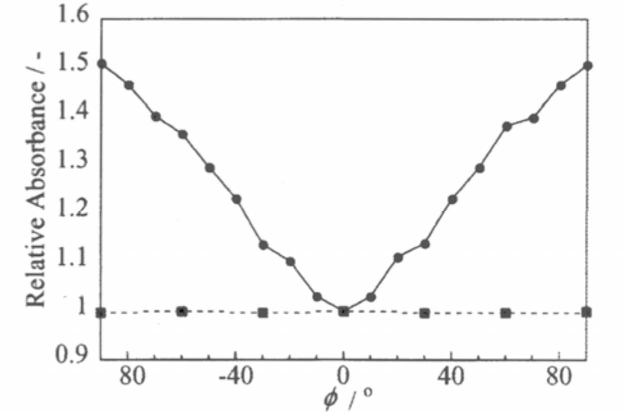
1.2 nm

+

Uniaxially Aligned Mesoporous Structure

■ **Alignment Control of Cyanine Dye**

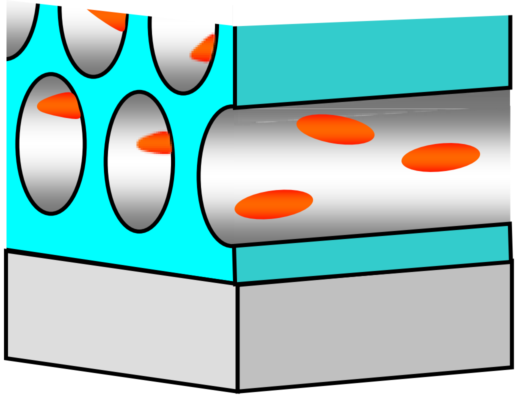
Polarization Dependence



● **Well-Aligned Mesochannles**

■ **Random Alignment Mesochannels**

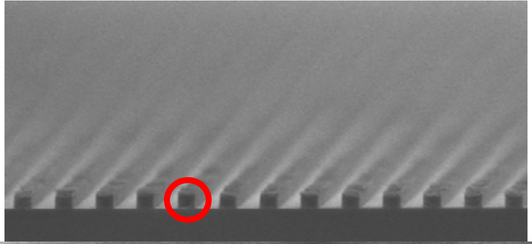
Model

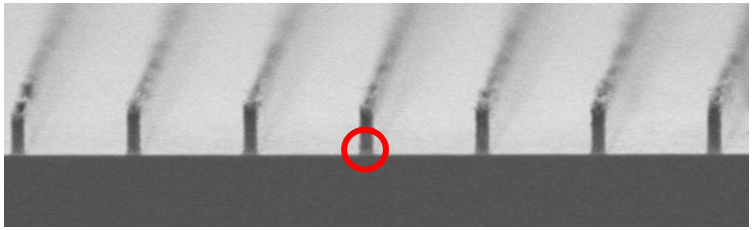


Fukuoka, A., Kuroda, K., *Chem. Conmn.*, **2003**, 284.

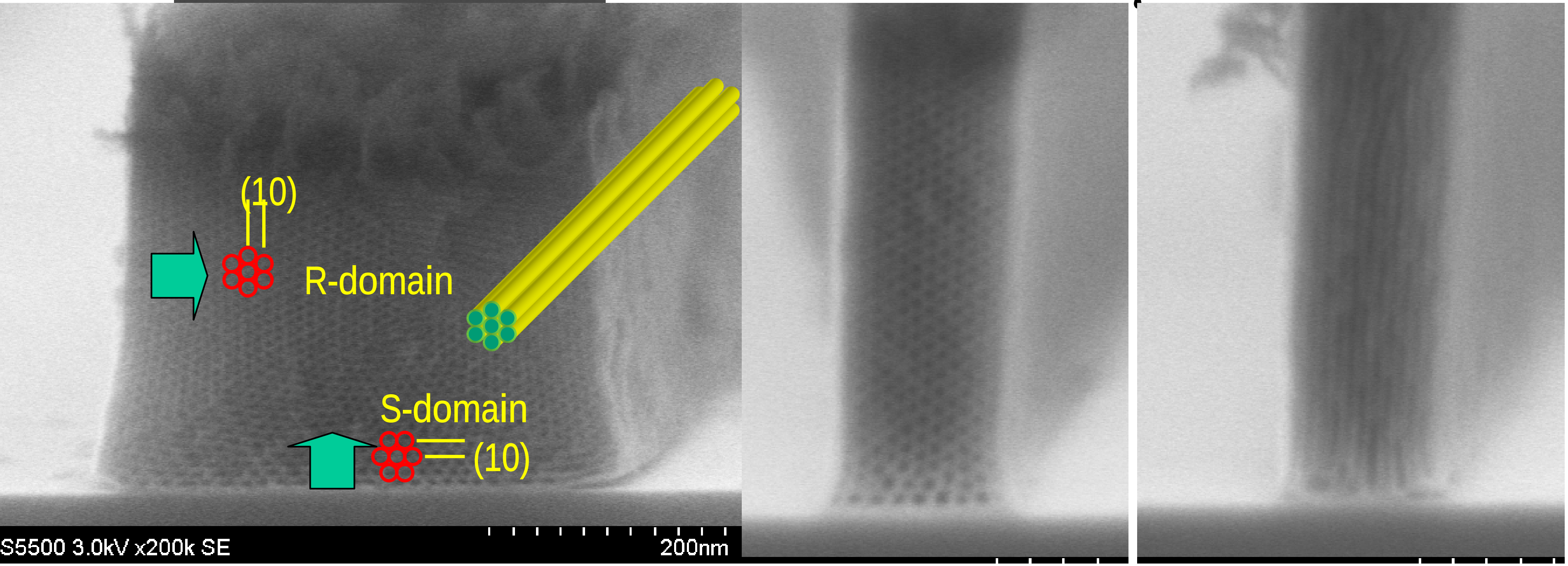
Orientation of mesochannels in line patterns

0.5-μm line



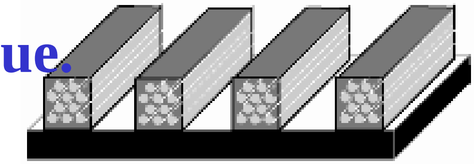


0.1-μm line



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

Possibly exceeding the limitation of lithography technique.



C. W. Wu, K. Kuroda et al., *Angew. Chem. Int. Ed.* **46**, 5364 (2007).

OUTLINE

Background

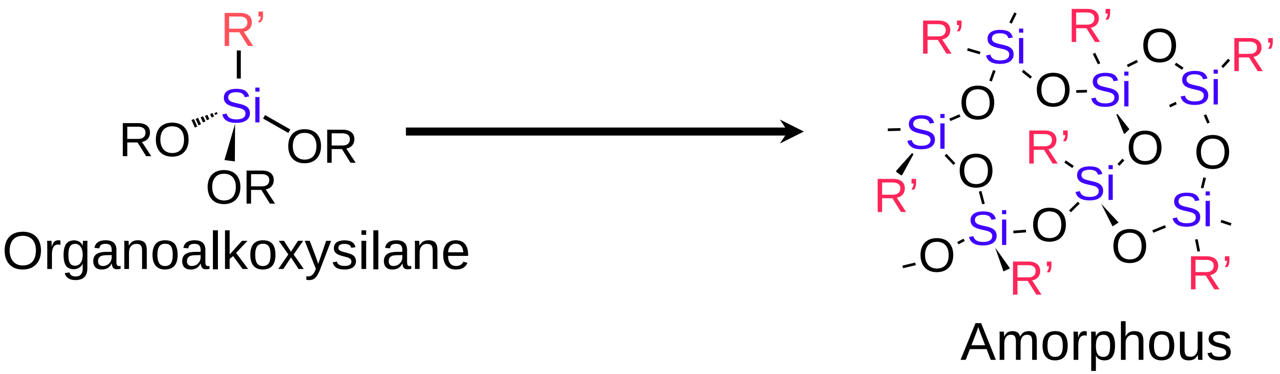
Mesoporous materials

Mesoporous films utilizing alkoxysilanes

<u>Design of alkoxysilanes and self-assembly</u>

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

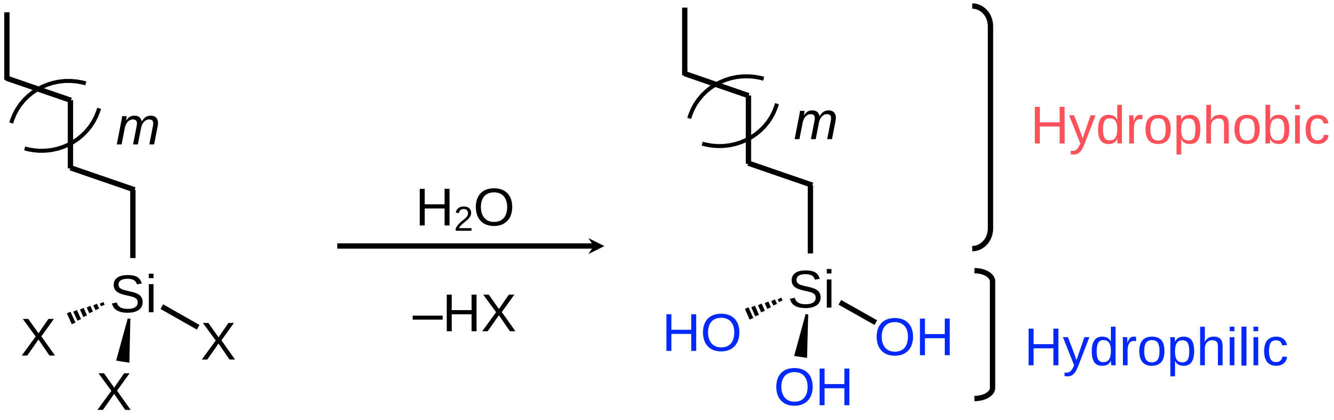
Novel hybrid materials with unique nanostructures and properties

Ordered arrangement of organic groups

Structural control of siloxane framework

Design of amphiphilic molecules

Example)



(X = OMe, OEt, Cl)

Amphiphilic molecules

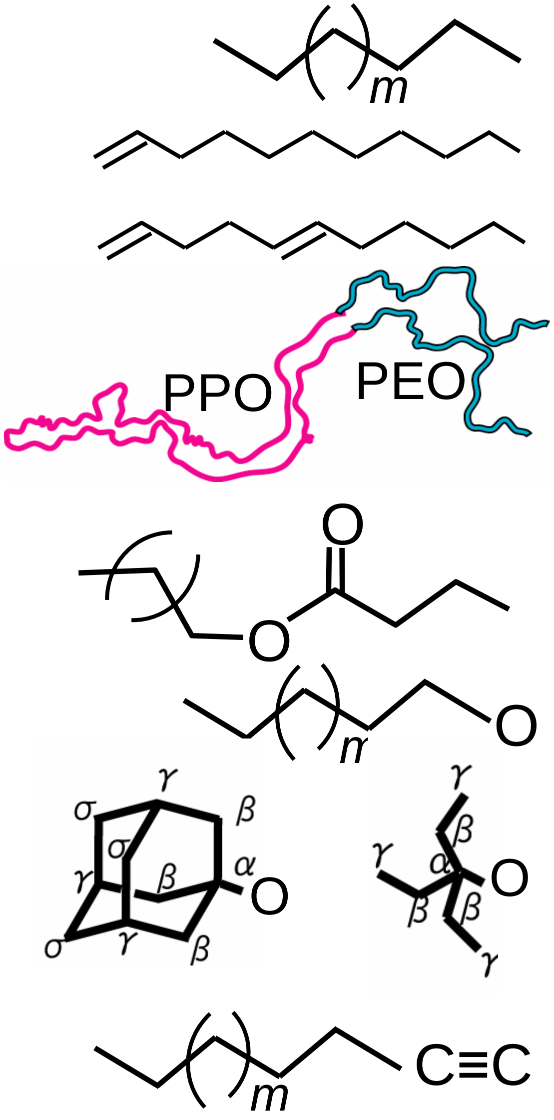
Self-Assembled Monolayers (SAMs) = 2D self-organization

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

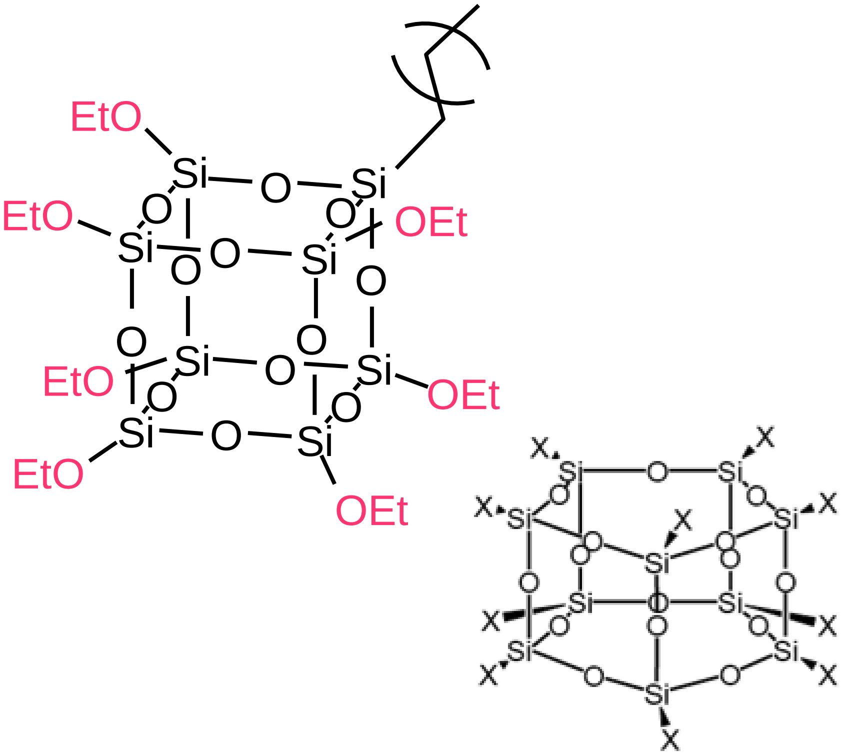
$R \text{———} Si\text{-}X_3$



$SiCl_3$

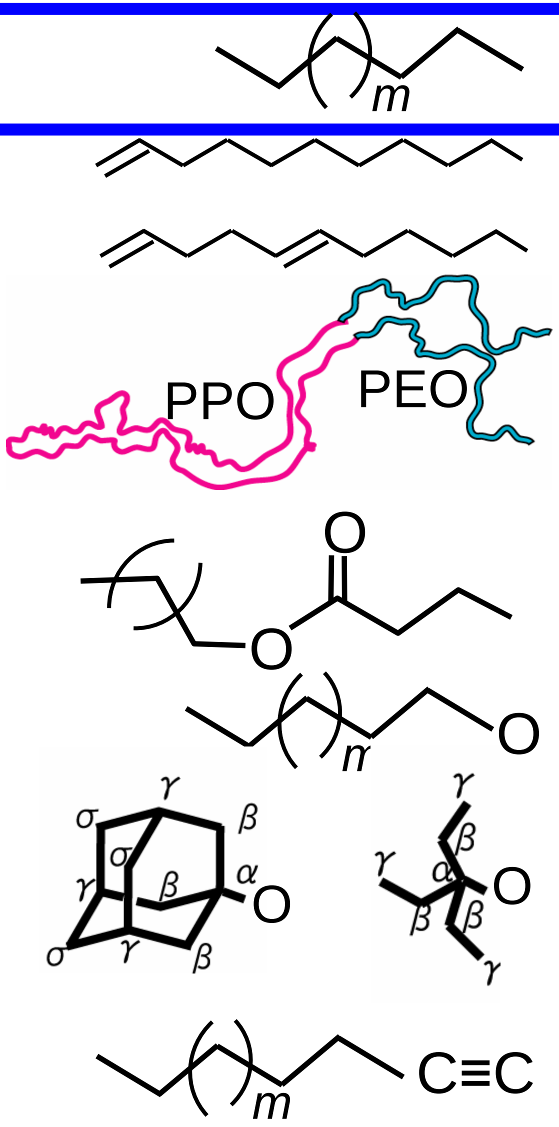
$Si(OR)_3$

$Si(OSi(OR)_3)_3$



Varieties in organosilanes

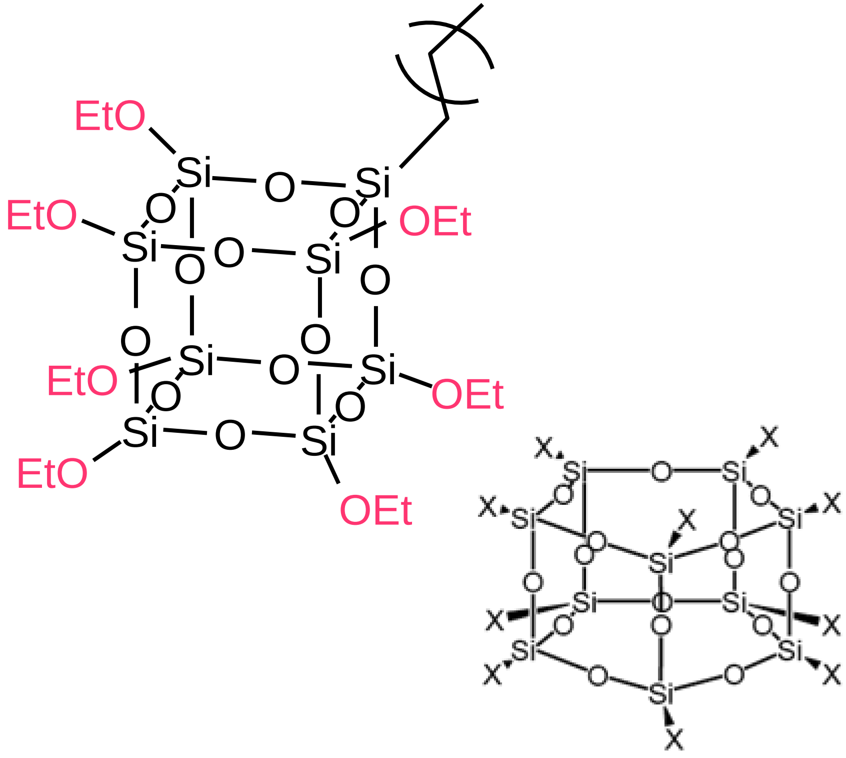
R —— $\mathrm{Si\text{-}X_3}$



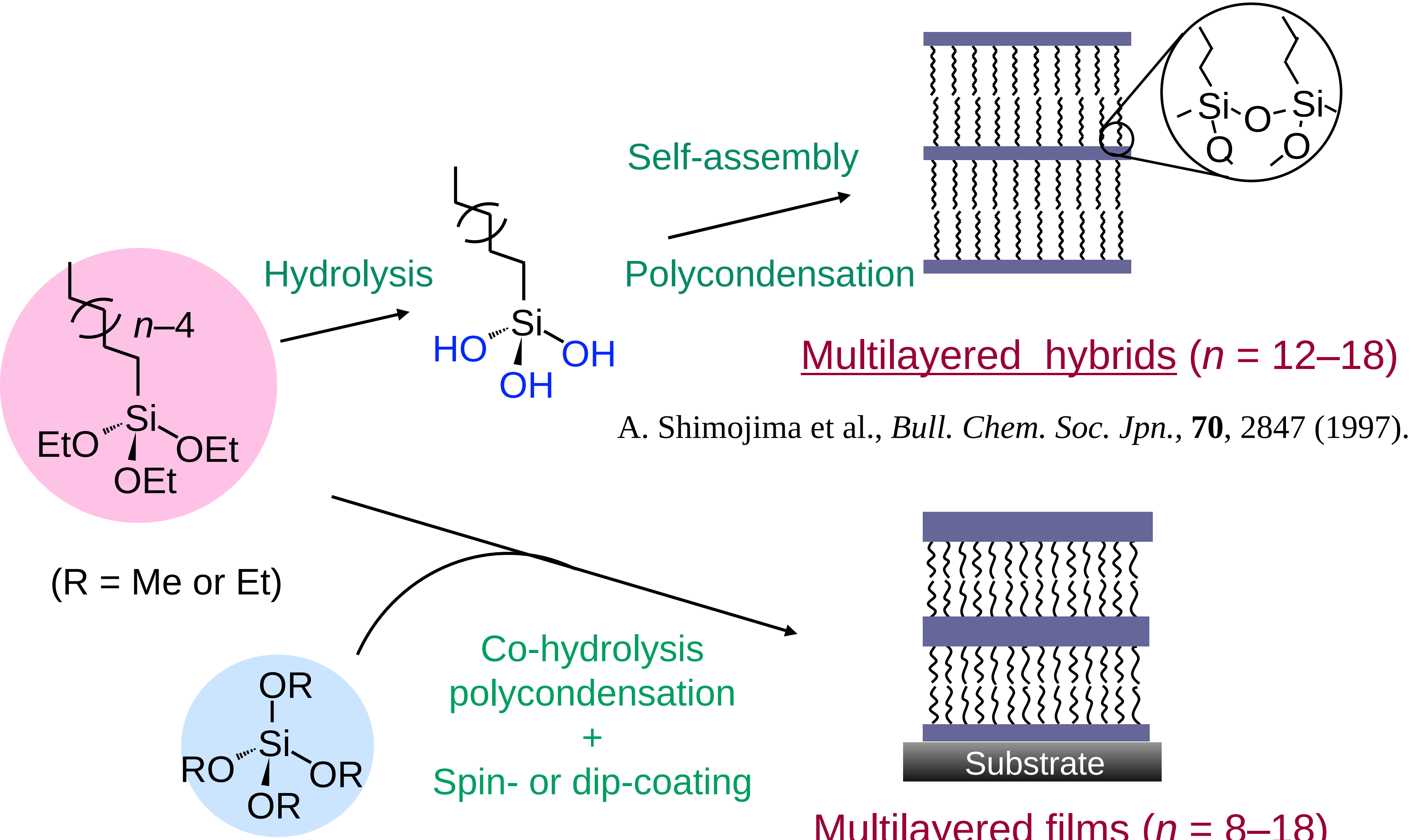
$\mathrm{SiCl_3}$

$\mathrm{Si(OR)_3}$

$\mathrm{Si(OSi(OR)_3)_3}$



Our previous works



Hydrolysis

Self-assembly

Polycondensation

Multilayered hybrids (*n* = 12–18)

A. Shimojima et al., *Bull. Chem. Soc. Jpn.*, **70**, 2847 (1997).

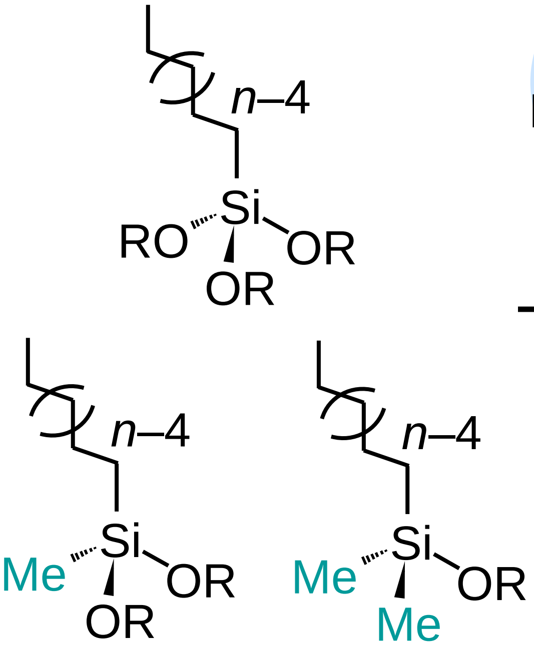
(R = Me or Et)

Co-hydrolysis
polycondensation
+
Spin- or dip-coating

Multilayered films (*n* = 8–18)

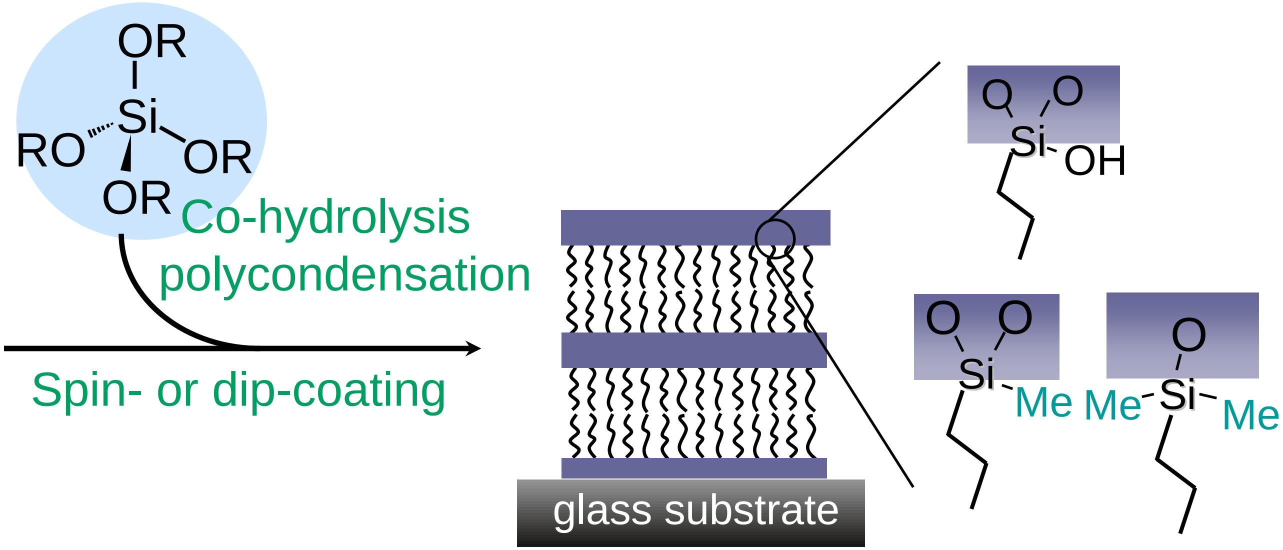
A. Shimojima et al., *J. Am. Chem. Soc.*, **120**, 4580 (1998).
Langmuir, **18**, 1144 (2002).

Formation of Layered Hybrid Films



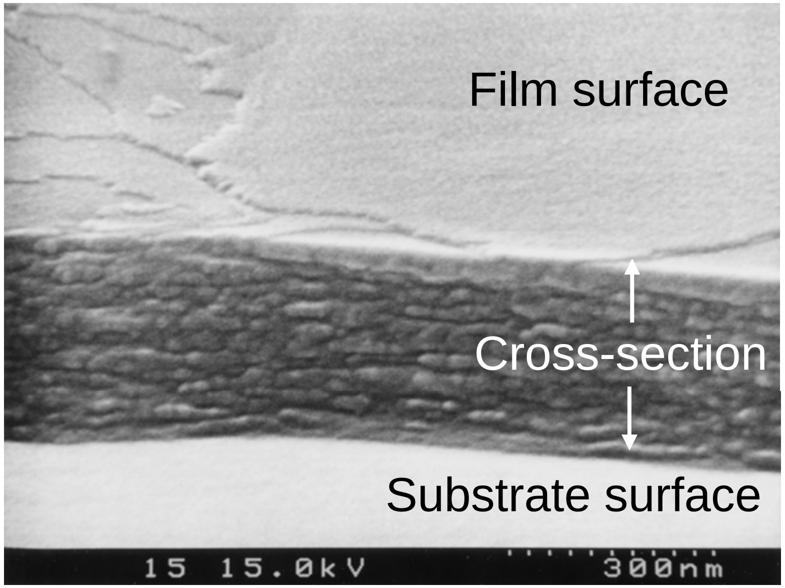
(R = Me or Et)

(n = 8–18)



$C_{18}H_{37}Si(OEt)_3$: TEOS = 1 : 4

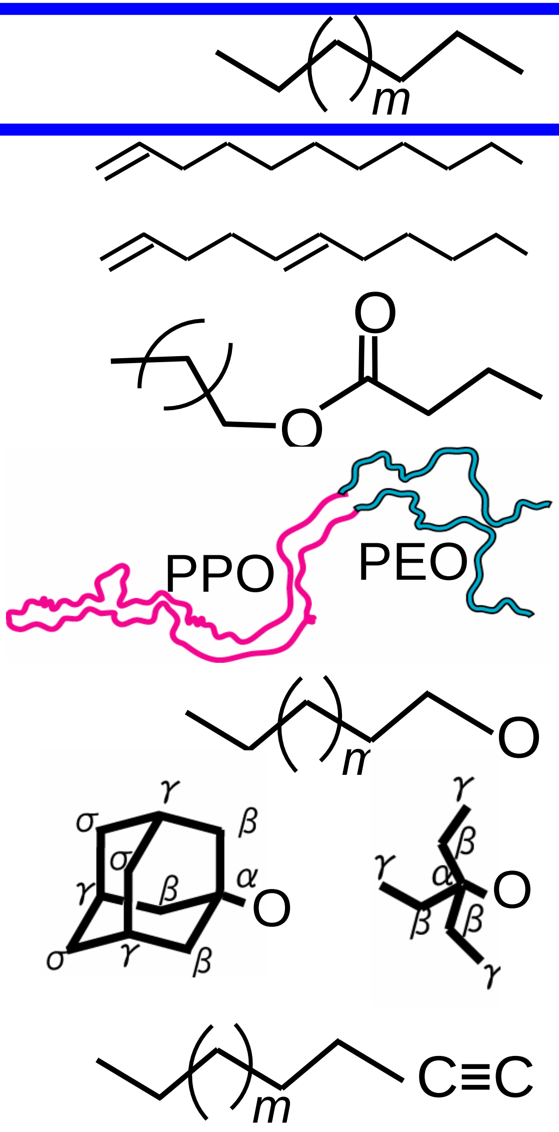
Cross-sectional SEM image



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

Varieties in organosilanes

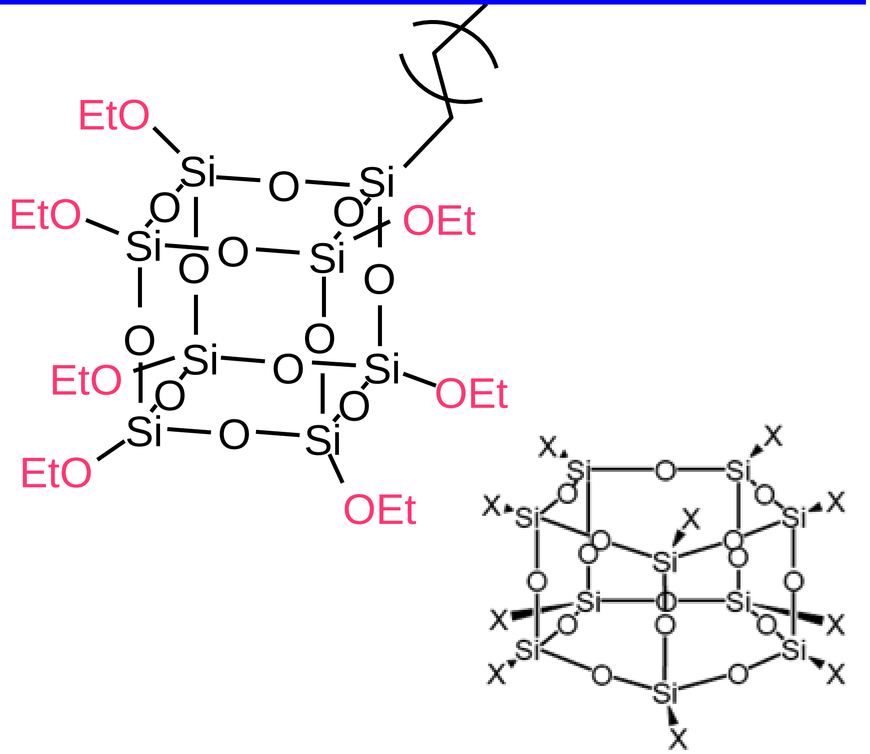
R —— Si-X$_3$



$SiCl_3$

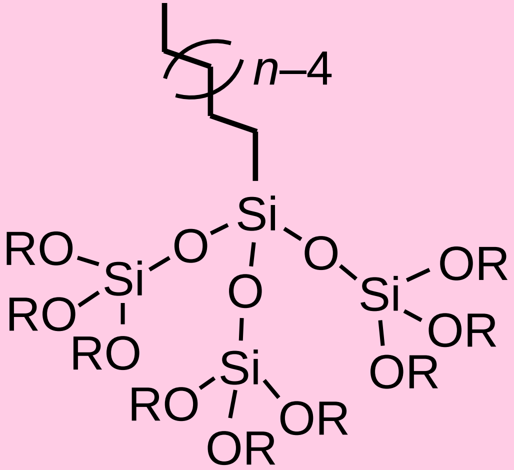
$SiOR_3$

$Si(OSi(OR)_3)_3$



Molecular Design of Oligosiloxane Precursors

Novel siloxane oligomers with alkyl chains
= <u>single precursors</u>



R = Me

<u>**1**(C*n*) (*n* = 4–18)</u>

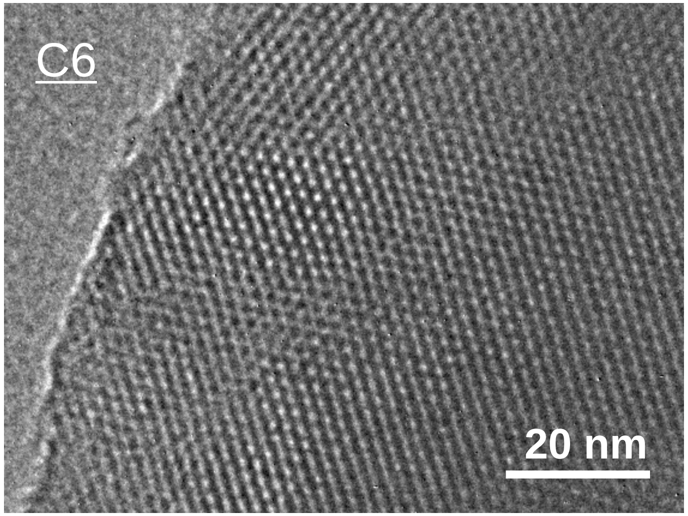
Well-defined molecular shape
Self-assembling ability
High network-forming ability

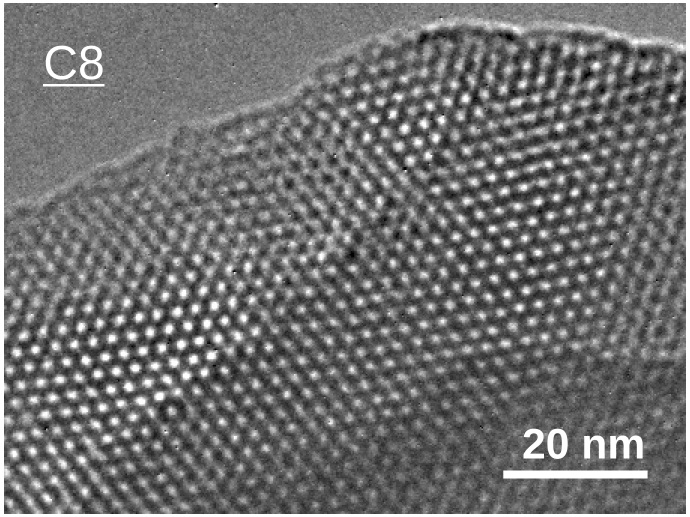
Better control of

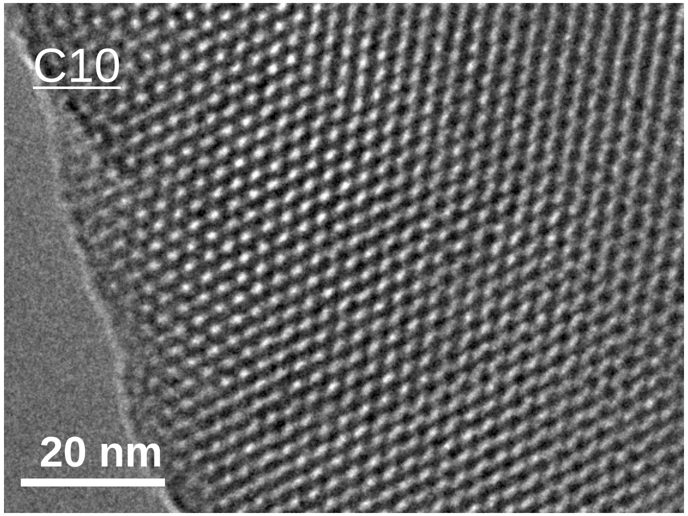
- Reaction process
- Nanostructure & morphology of the products

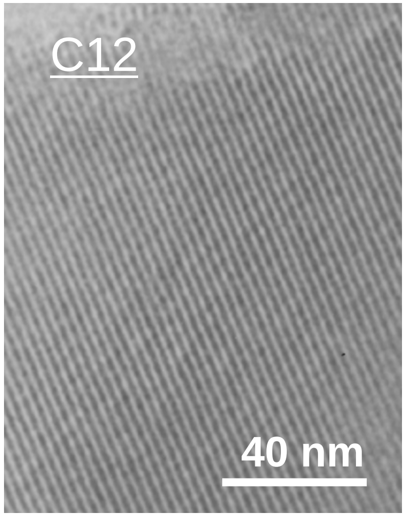
Angew. Chem. Int. Ed., **42**, 4057 (2003).

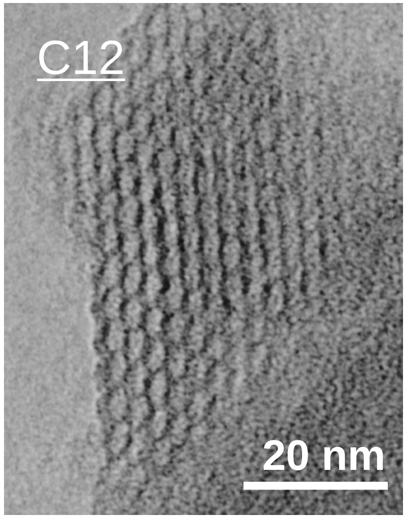
TEM Images (as-made samples)





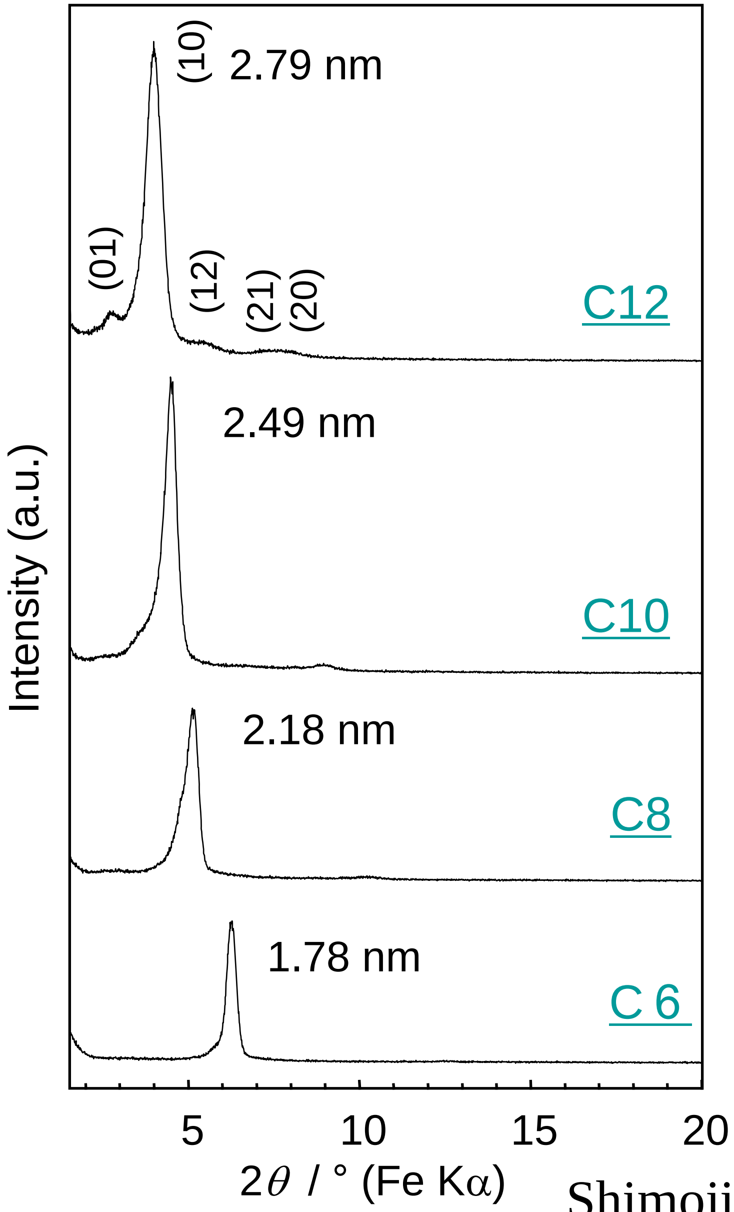


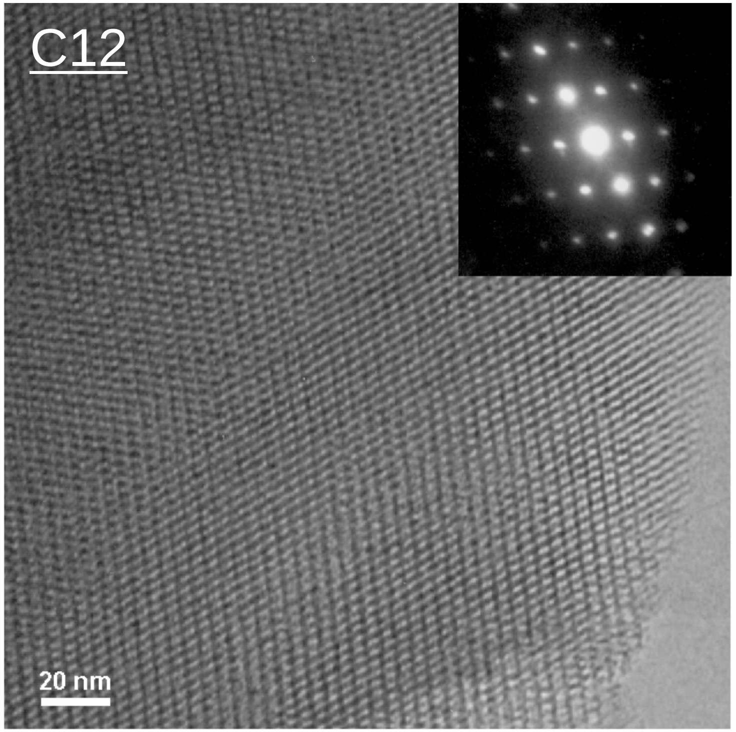


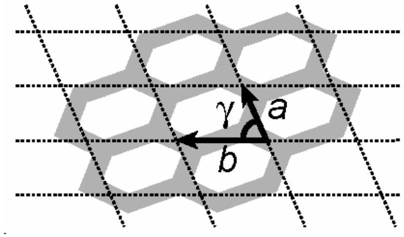


Shimojima, Liu, Ohsuna,Terasaki, Kuroda, JACS (2005)

XRD Patterns (calcined samples)



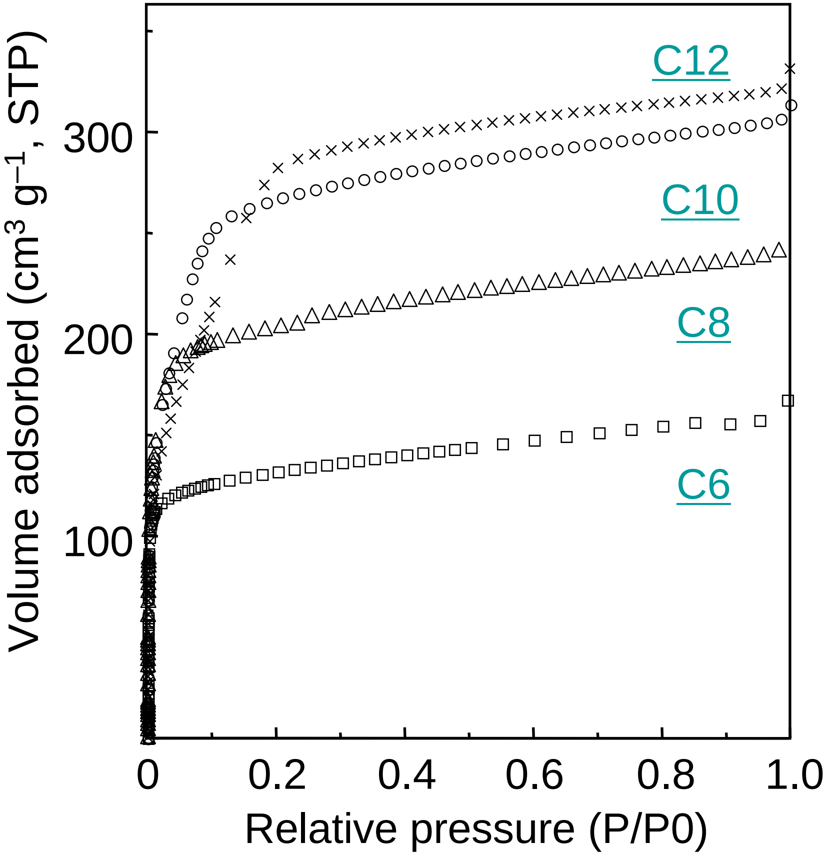




2D monoclinic structure

Shimojima, Liu, Ohsuna,Terasaki, Kuroda, JACS (2005)

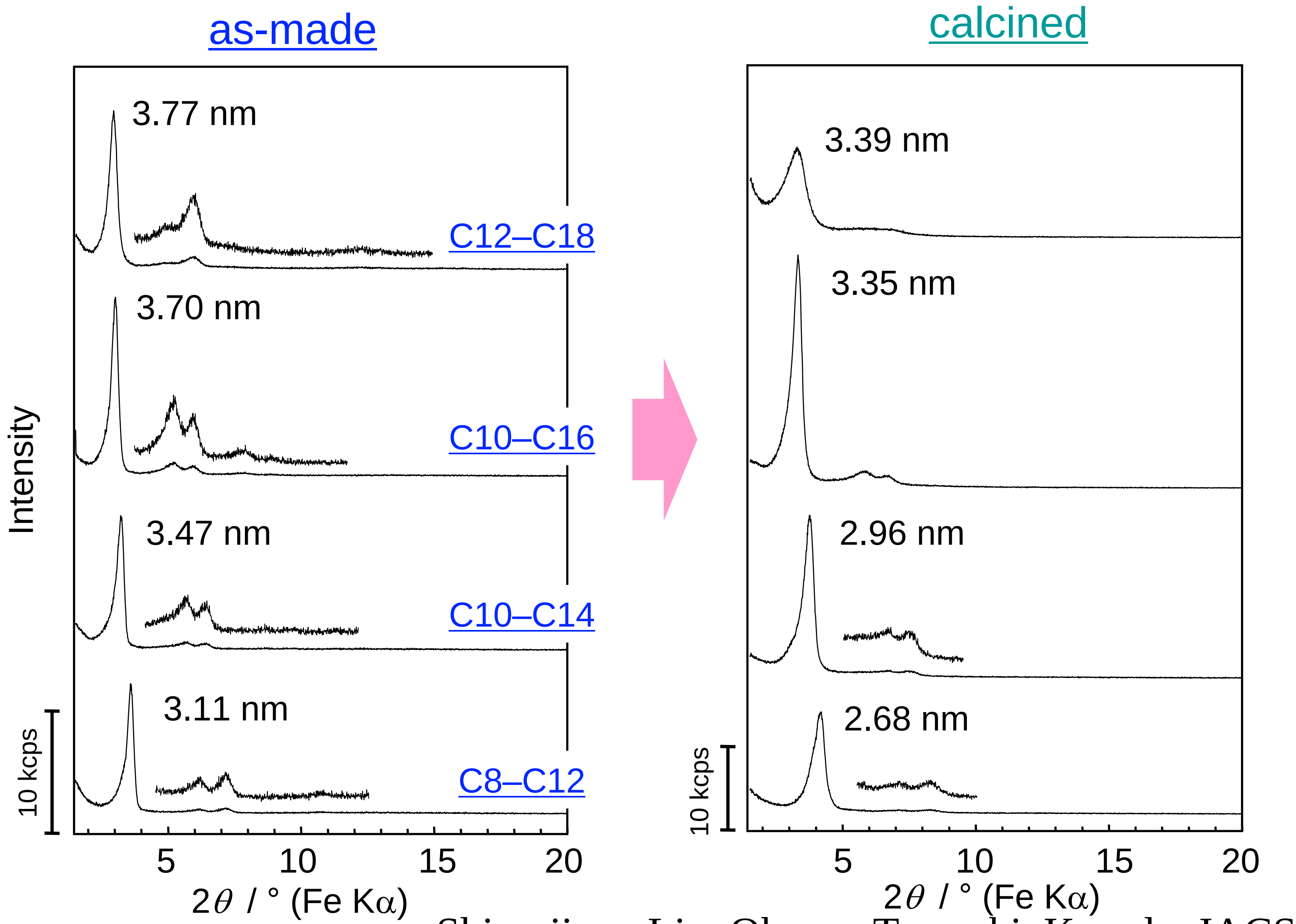
N_2 adsorption isotherms (calcined samples)



n	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

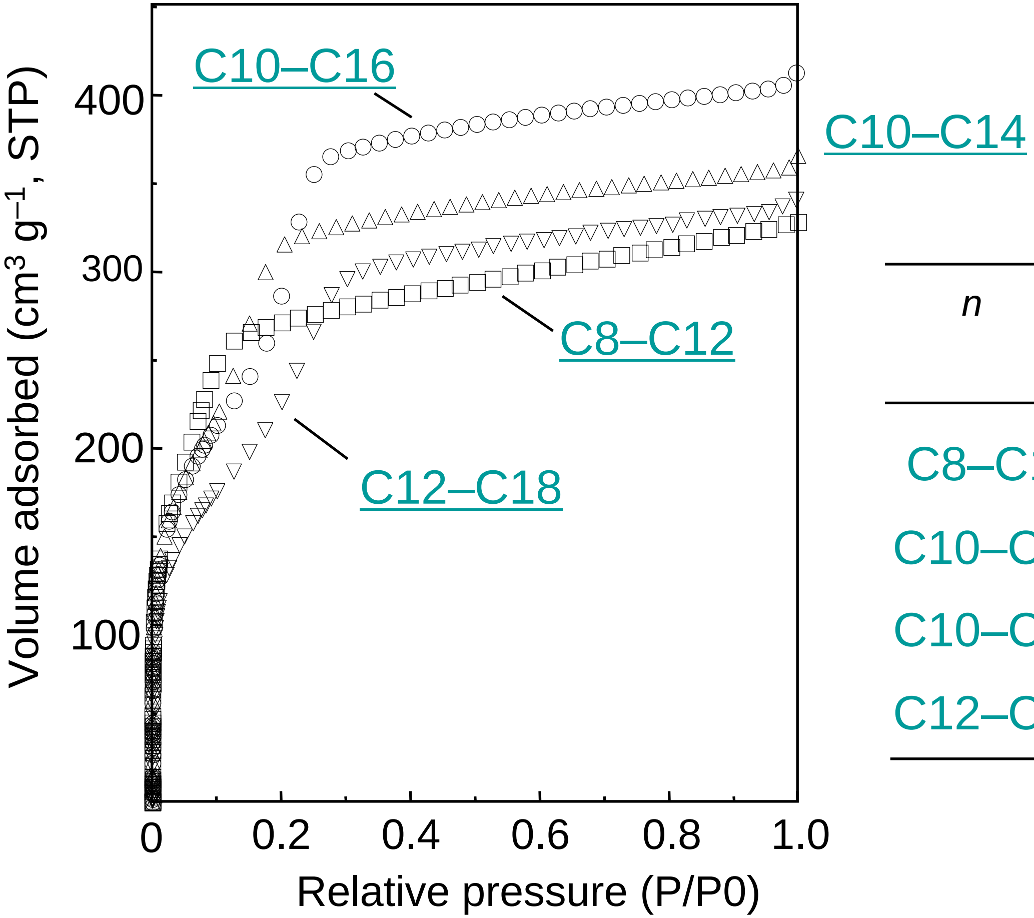
Shimojima, Liu, Ohsuna,Terasaki, Kuroda, JACS (2005)

XRD Patterns - Binary systems of 1(C*n*) with different chain lengths -



Shimojima, Liu, Ohsuna,Terasaki, Kuroda, JACS (2005)

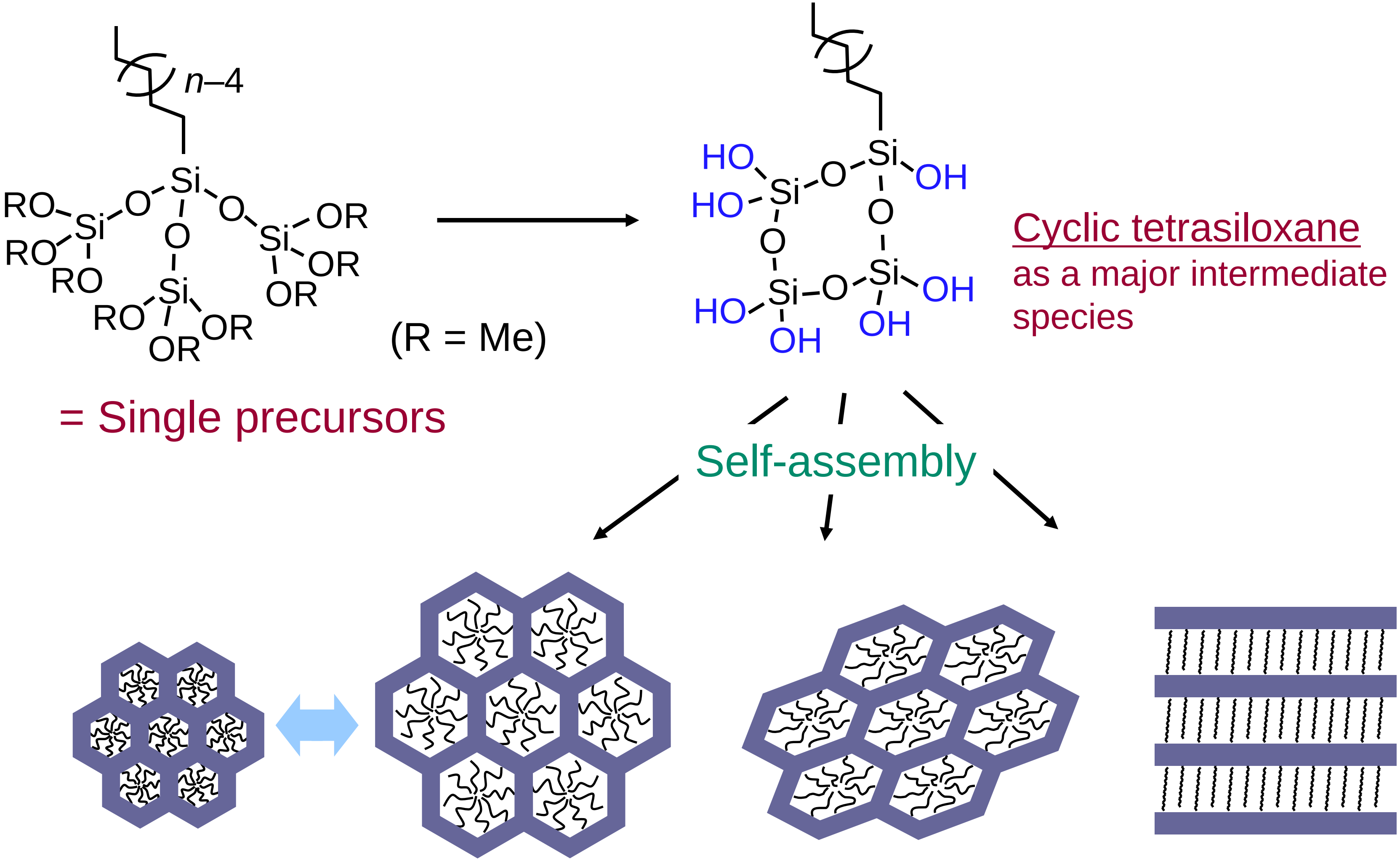
N_2 adsorption isotherms (calcined samples)



n	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

Shimojima, Liu, Ohsuna,Terasaki, Kuroda, JACS (2005)

Self-assembly processes of 1(C*n*)



(R = Me)

= Single precursors

Cyclic tetrasiloxane
as a major intermediate
species

Self-assembly

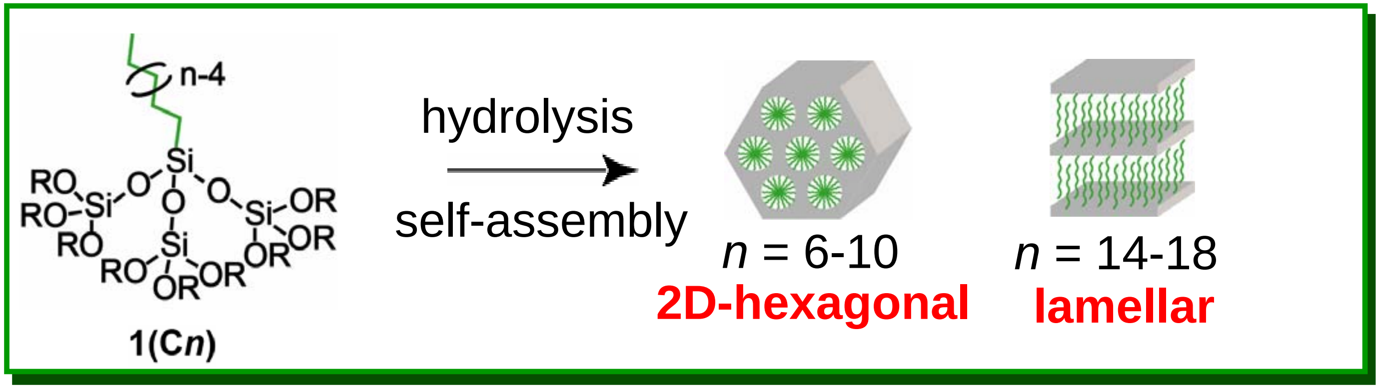
(*n* = 6–10, *n* = 10+16 etc.)
2D Hexagonal

(*n* = 12)
2D Monoclinic

(*n* = 14–18)
Lamellar

Shimojima, Liu, Ohsuna,Terasaki, Kuroda, JACS (2005)

Mesostrucured Siloxane-Organic Hybrid Films with Ordered Macropores



1(C*n*)

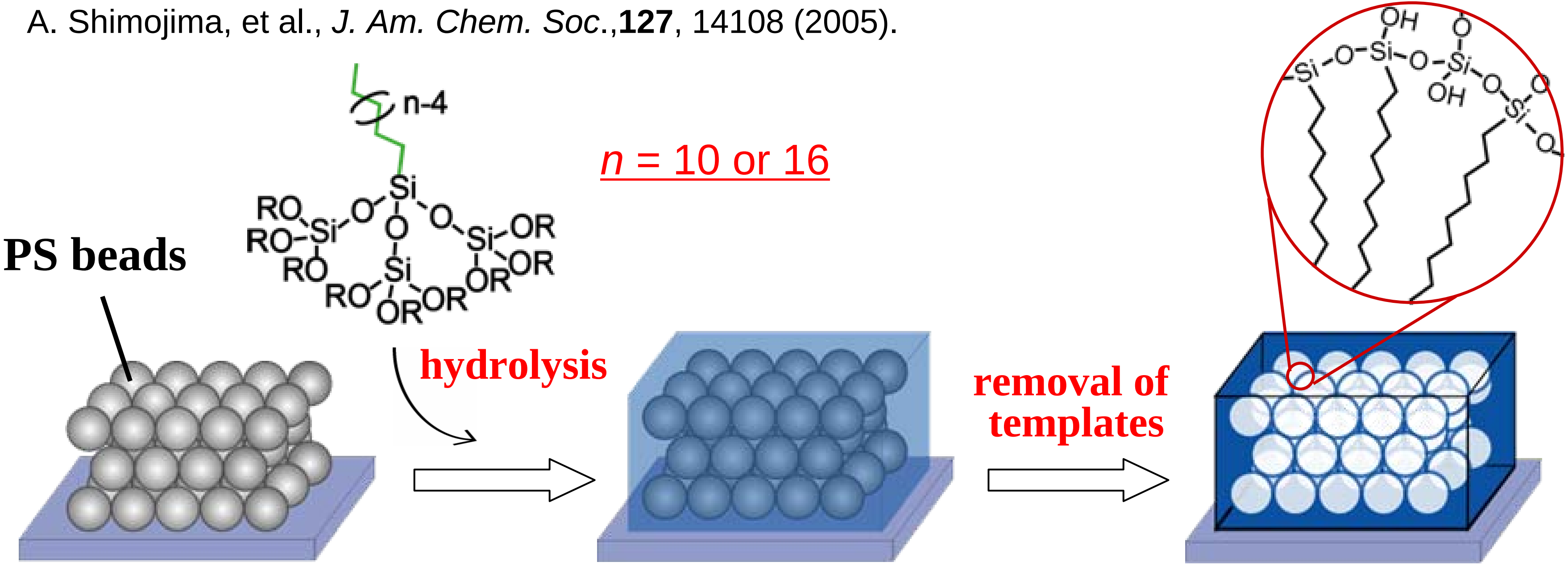
hydrolysis

self-assembly

n = 6-10
2D-hexagonal

n = 14-18
lamellar

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



n = 10 or 16

PS beads

hydrolysis

removal of templates

PS opal

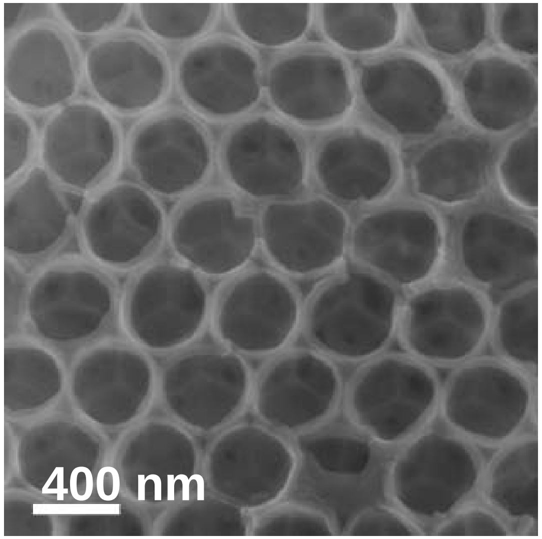
PS beads-hybrid composite

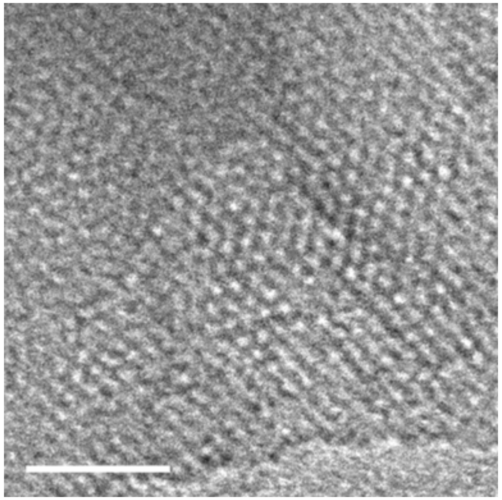
Inverse opal

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

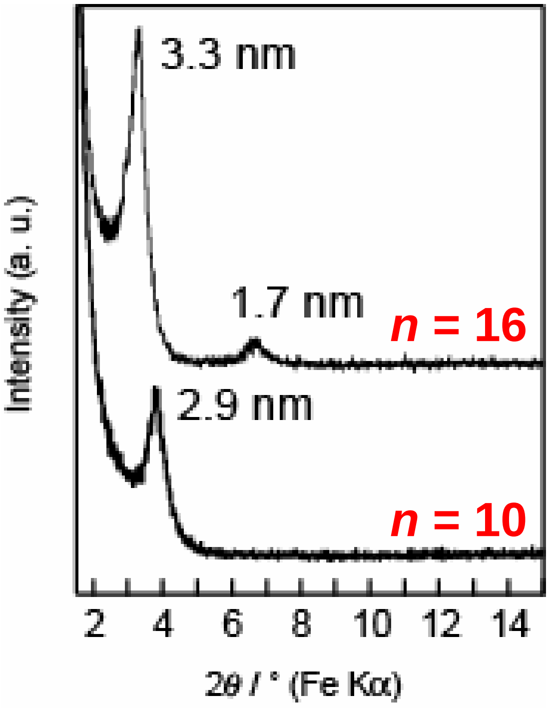
Inverse opal film

《*n* = 10》

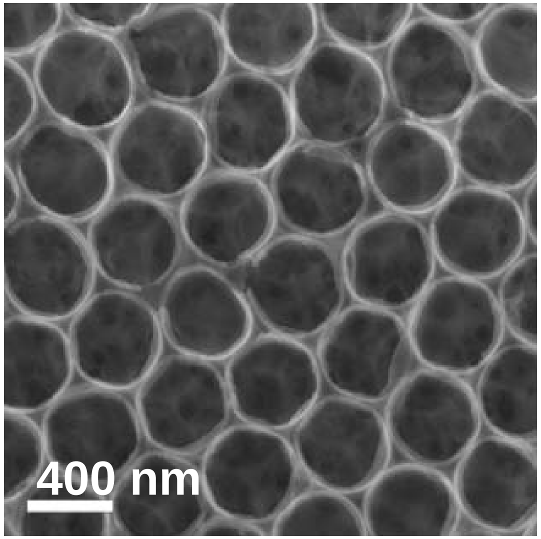


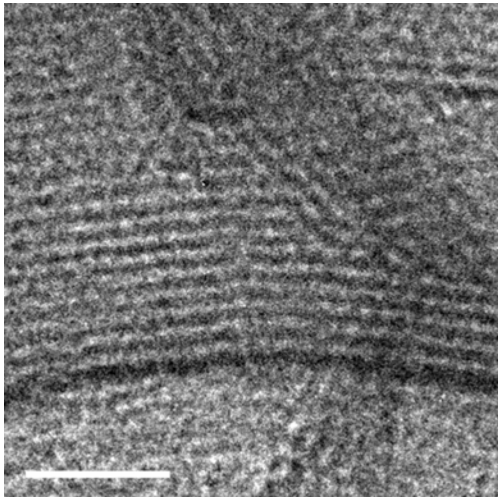


n = 10



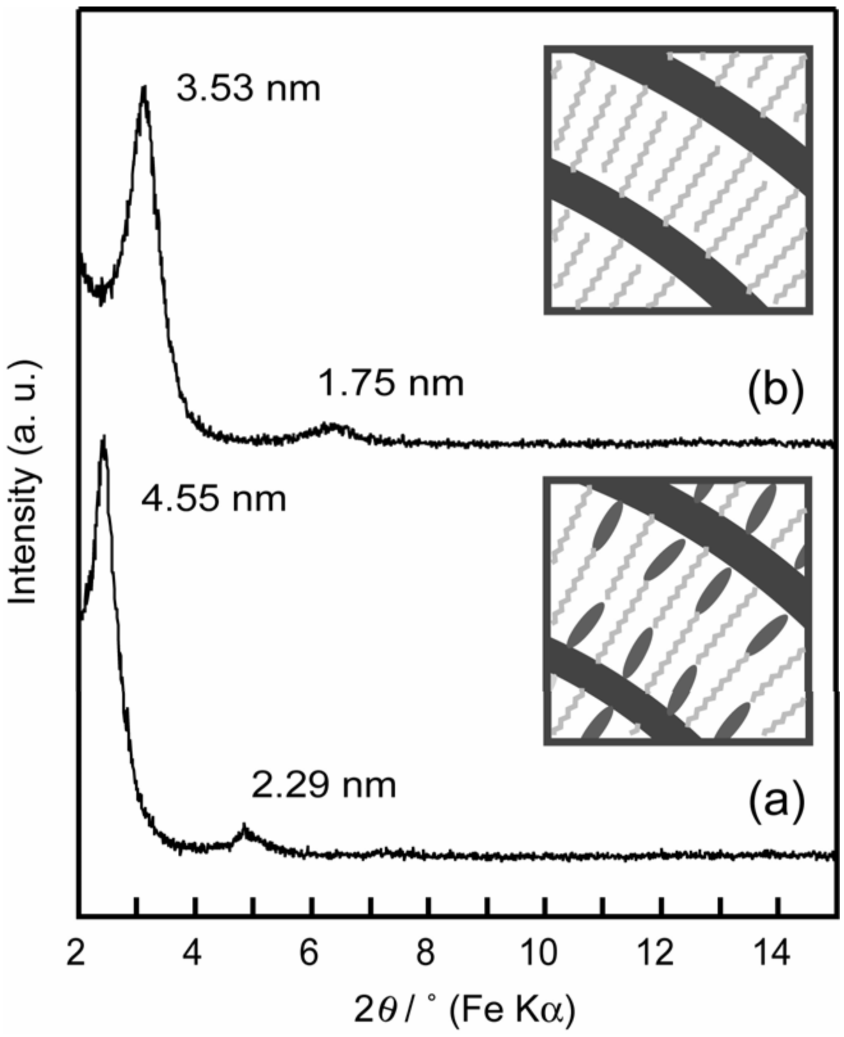
《*n* = 16》

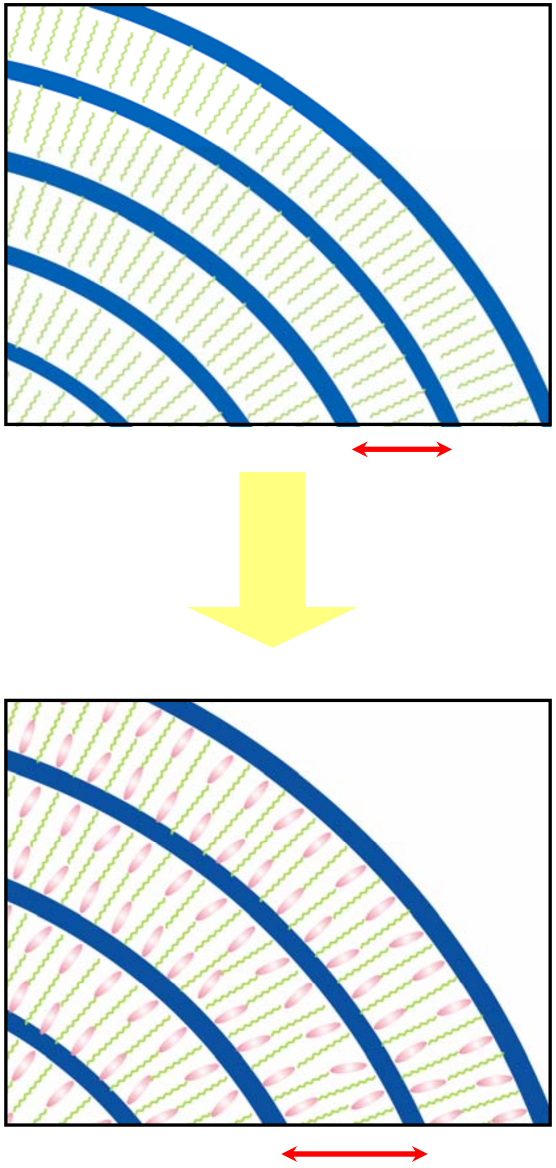




n = 16

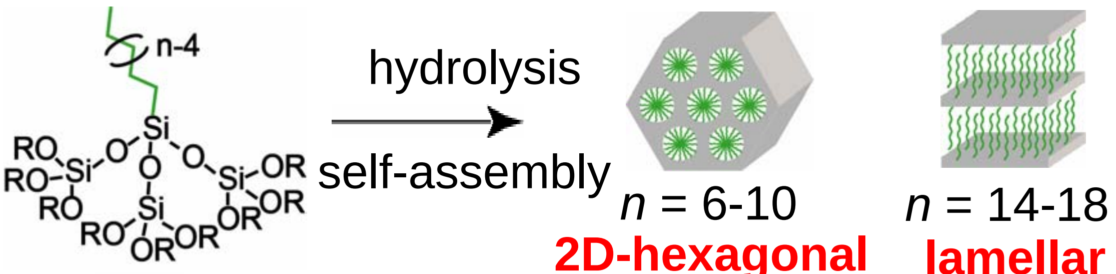
Intercalation of decyl alcohol





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

Synthesis of Siloxane-Organic Hybrid Nanorods



hydrolysis

self-assembly

n = 6-10

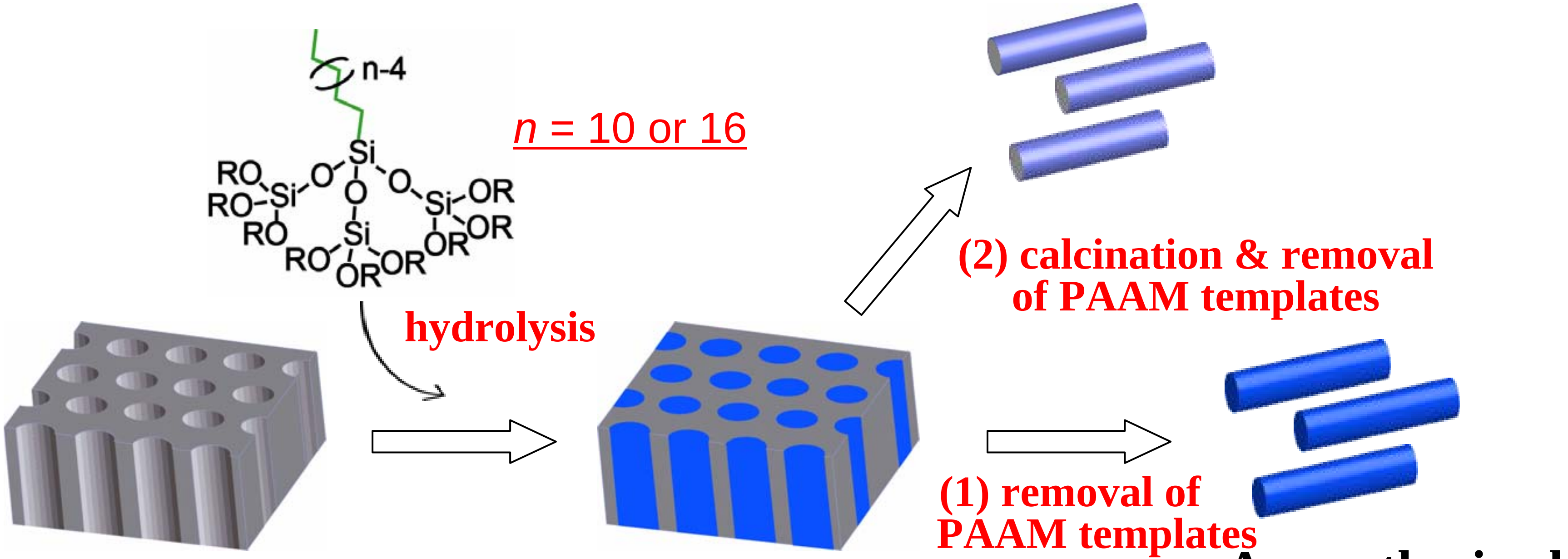
2D-hexagonal

n = 14-18

lamellar

1(C*n*)

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



Calcined nanorods

n = 10 or 16

hydrolysis

(2) calcination & removal of PAAM templates

(1) removal of PAAM templates

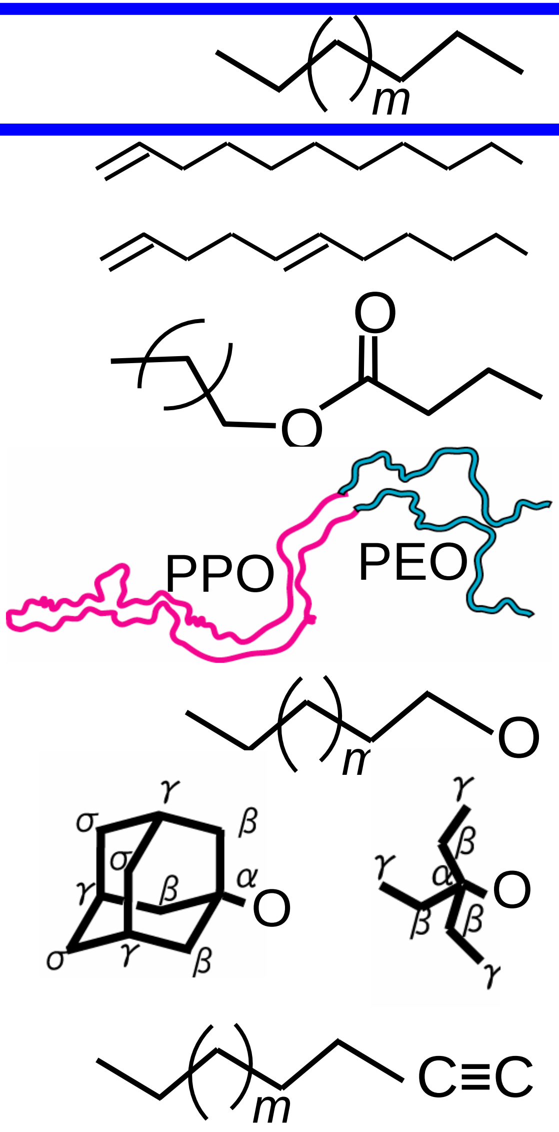
PAAM

PAAM – hybrid composite

As-synthesized nanorods

Varieties in organosilanes

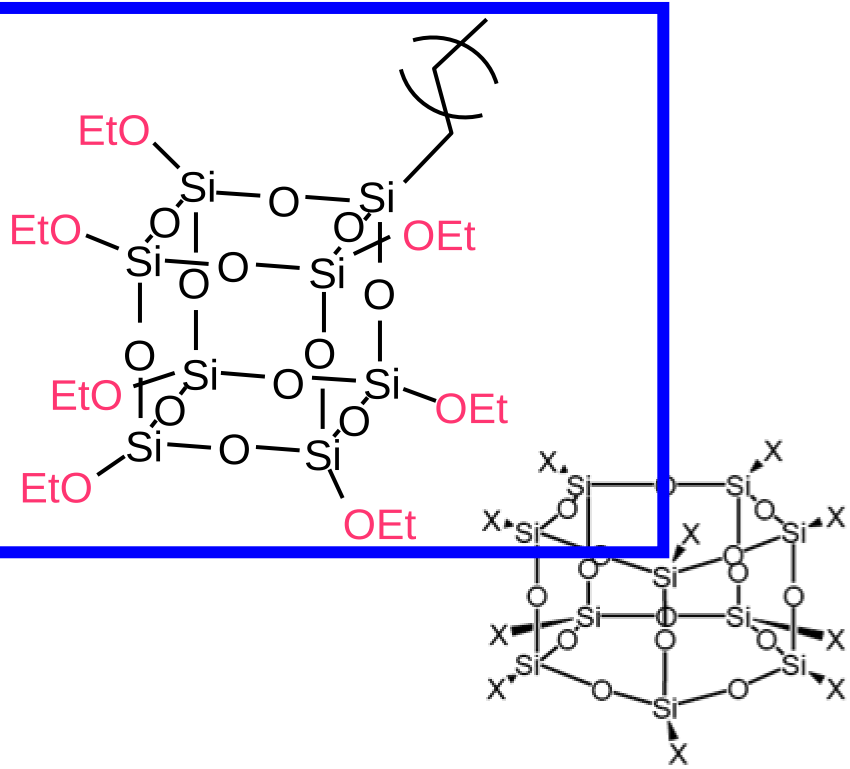
$$R \text{ —— } Si\text{-}X_3$$

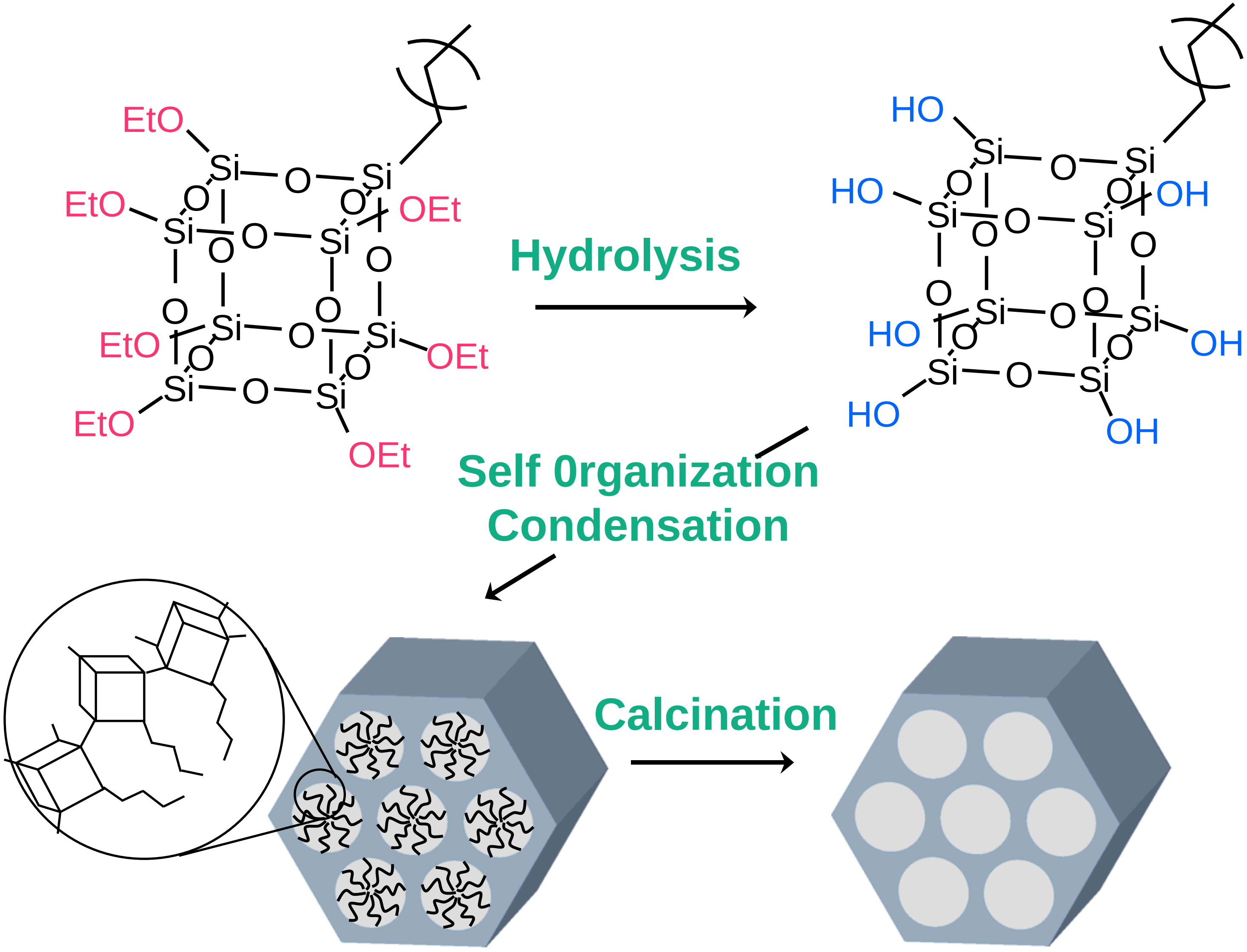


$SiCl_3$

$Si(OR)_3$

$Si(OSi(OR)_3)_3$





Hydrolysis

Self 0rganization Condensation

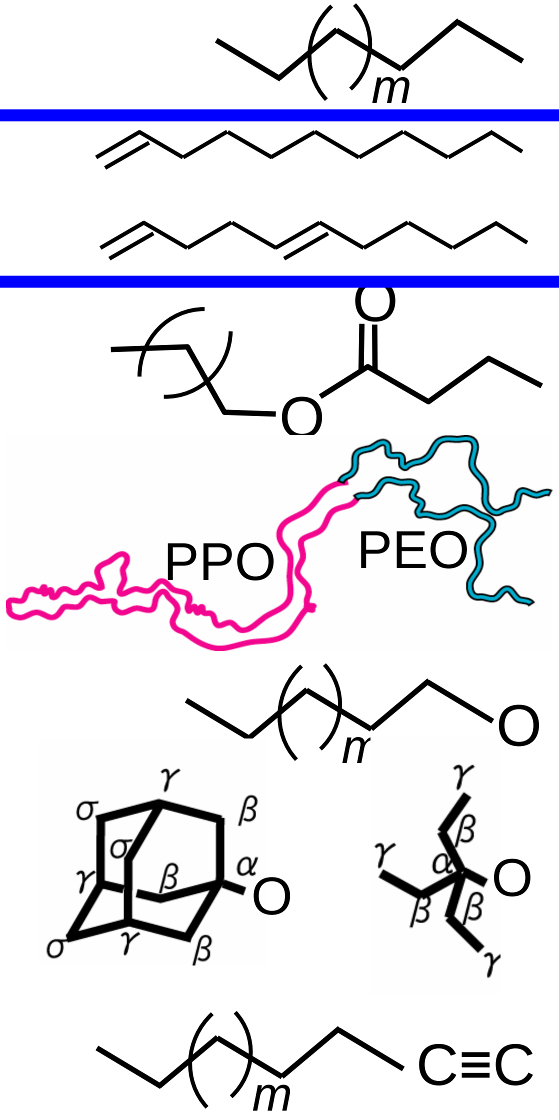
Calcination

Mestructured Hybrids
(2D hexagonal)

Mesoporous silica

Varieties in organosilanes

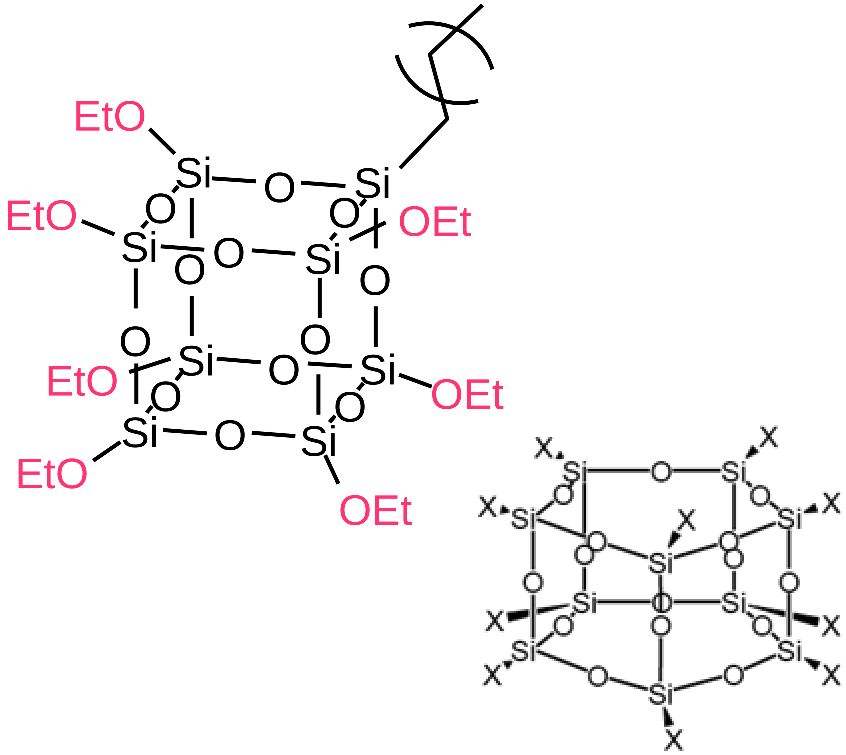
$$R —— Si\text{-}X_3$$



$SiCl_3$

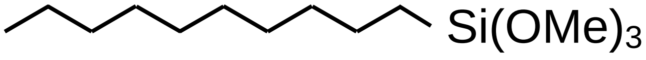
$SiOR_3$

$Si(OSi(OR)_3)_3$



This study

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



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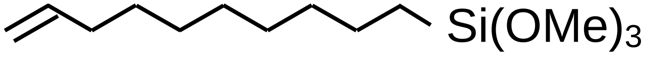
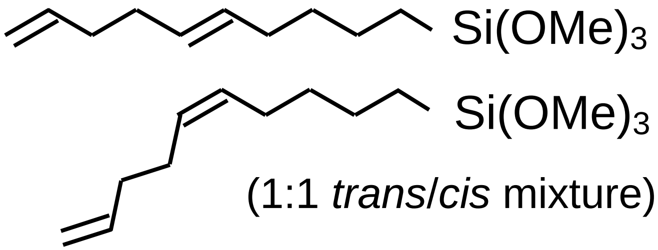


1



(1:1 *trans*/*cis* mixture)

2

Co-hydrolysis and polycondensation with $Si(OMe)_4$

Multilayered films (**L0**, **L1**, **L2**)

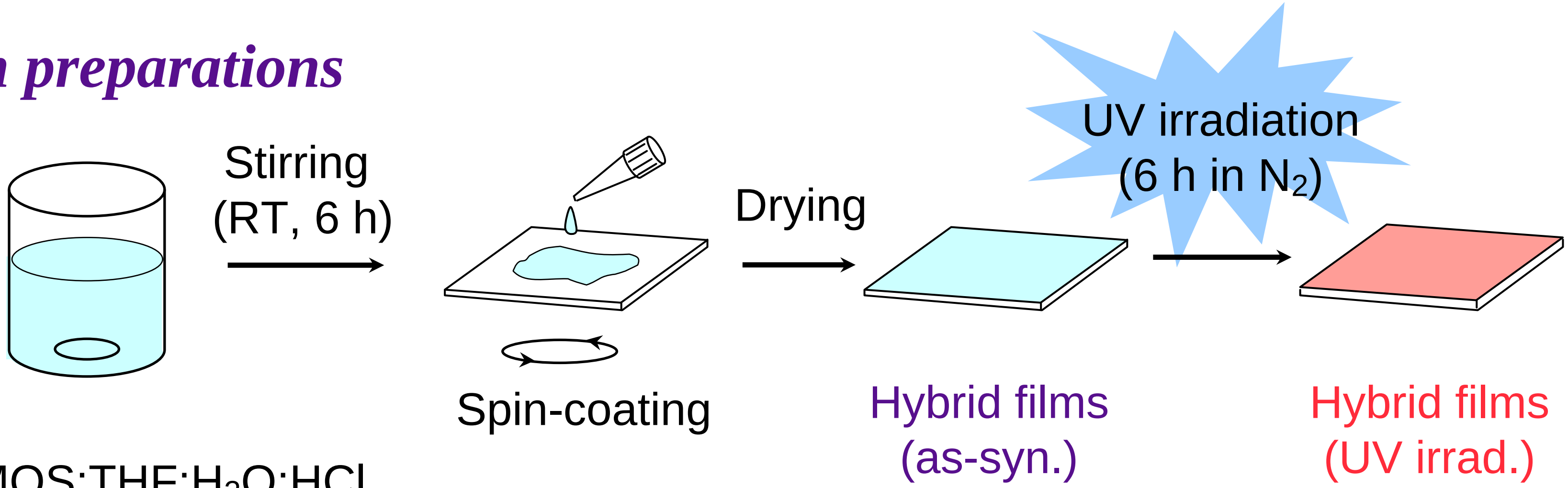
Disordered films (**D1**, **D2**)

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

→ Understanding of the structure–property relationships

Experimental

Film preparations



Stirring
(RT, 6 h)

Spin-coating

Drying

Hybrid films
(as-syn.)

UV irradiation
(6 h in N_2)

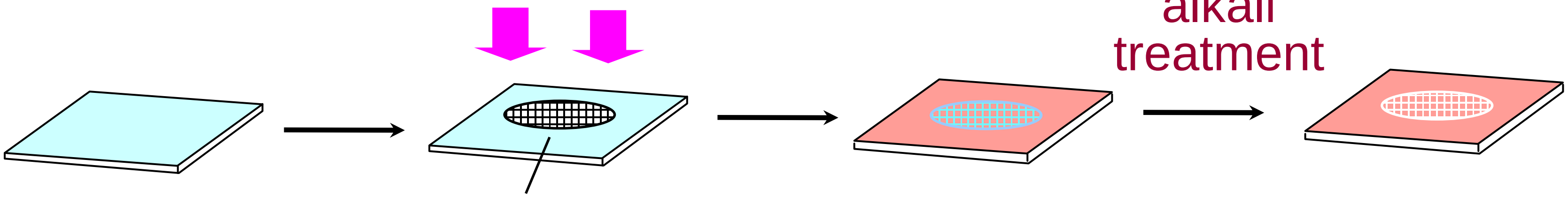
Hybrid films
(UV irrad.)

0–2:TMOS:THF:H_2O:HCl
= 1:4:15:19:0.002 (**L0**, **L1**, **L2**)
= 1:4:15:19:0.2 (**D1**, **D2**)

Analyses

^{29}Si NMR, XRD, IR, TEM, SEM, Nanoindentation test

Micropatterning



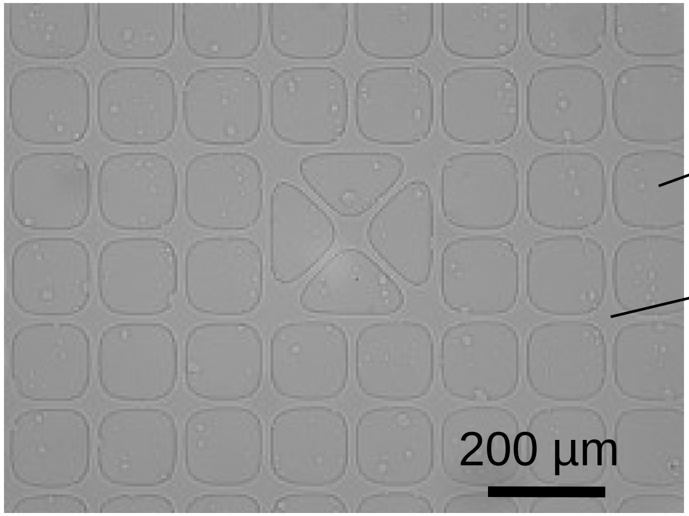
UV irradiation

alkali treatment

Hybrid film
(**L2**, as-syn.)

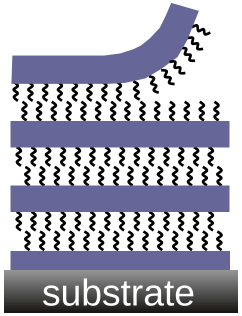
Cu TEM grid

Patterned film



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

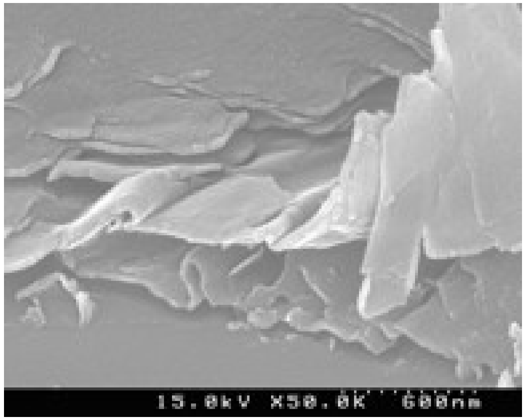
Structure–property relationships

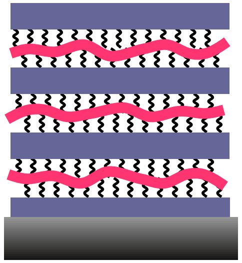


L0, L1, L2 (as-syn.)

× Hardness × Alkali resistance

No covalent bonds between adjacent layers (easily delaminated)



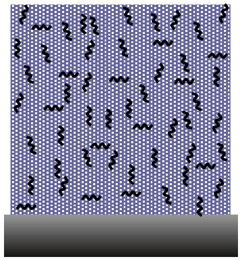


L1, L2 (UV irrad.)

◎ 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)



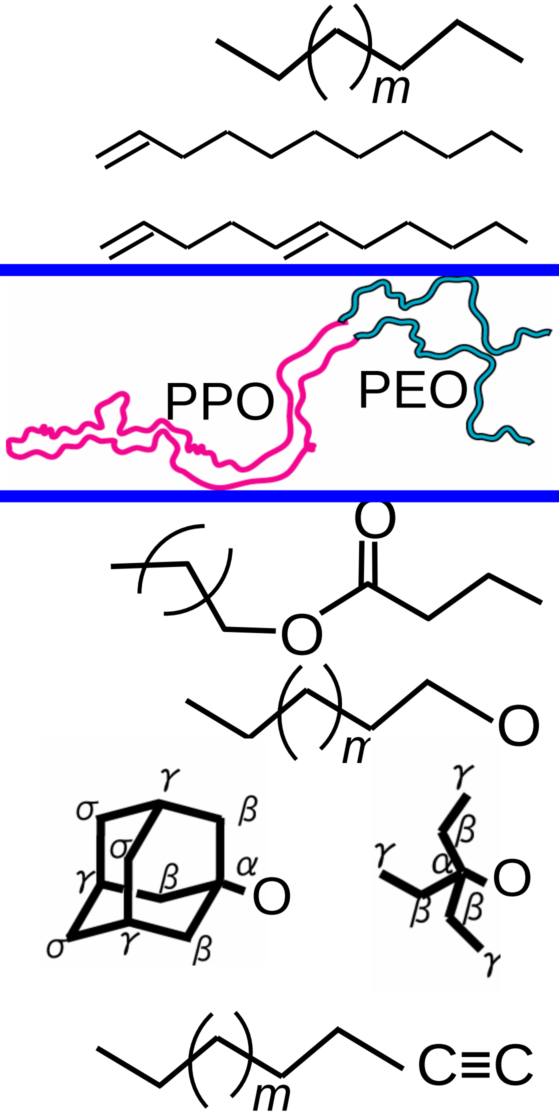
D1, D2

○ Hardness △ Alkali resistance

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

Varieties in organosilanes

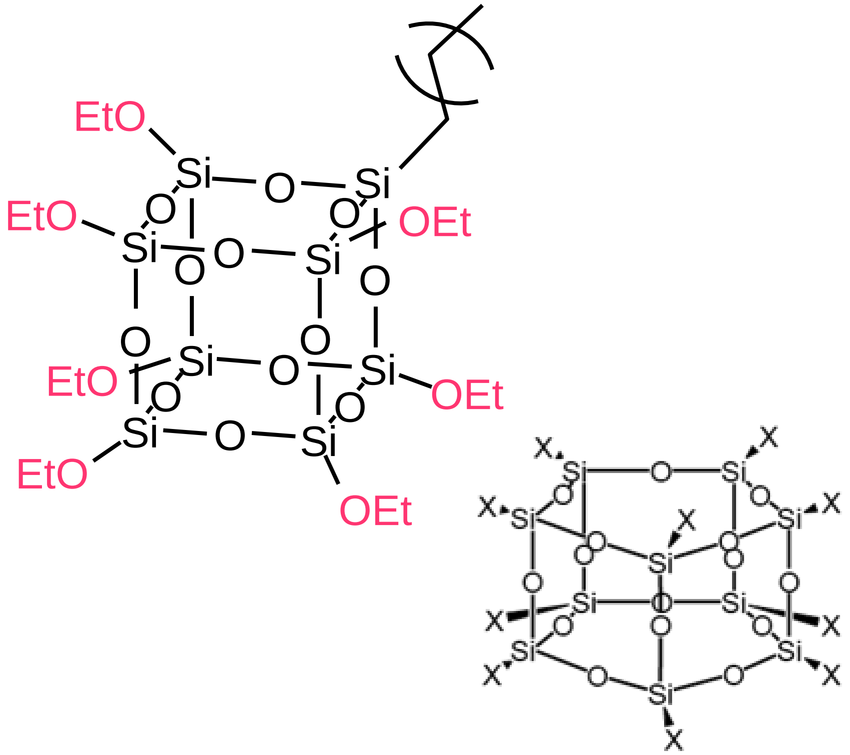
$R —— Si\text{-}X_3$



$SiCl_3$

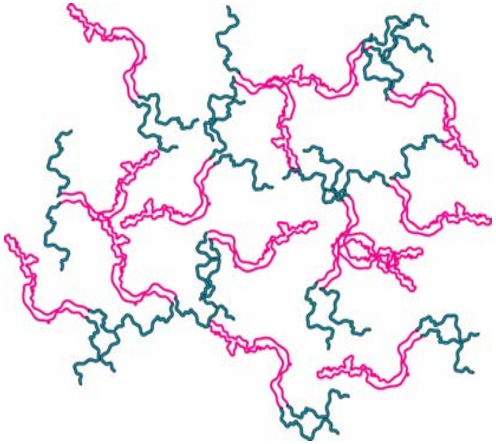
$SiOR_3$

$Si(OSi(OR)_3)_3$



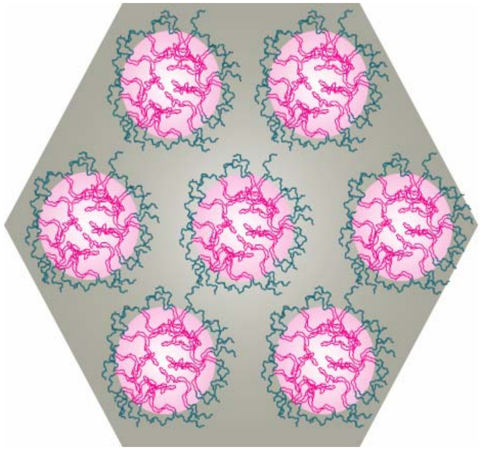
Structural design using inorganic and organic units

Supramolecular templating method



Self-assembly

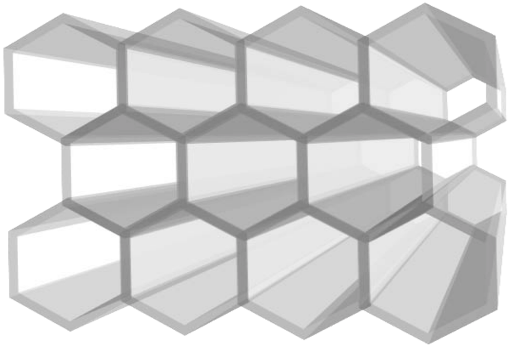
+ Inorganic species



Mesostructured materials

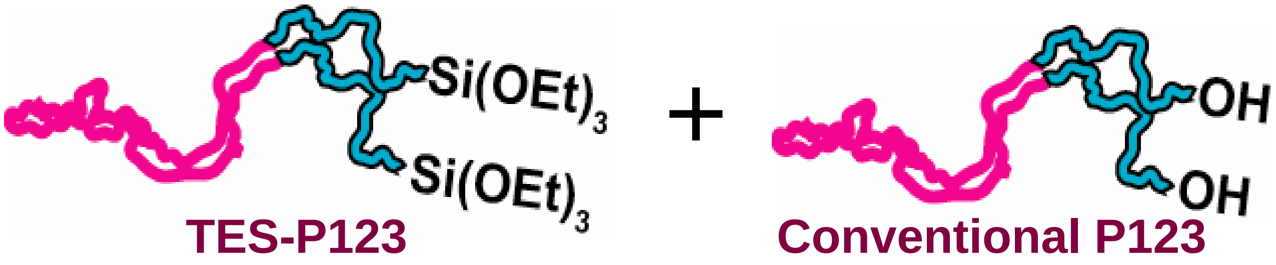
Mesoporous silicas

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



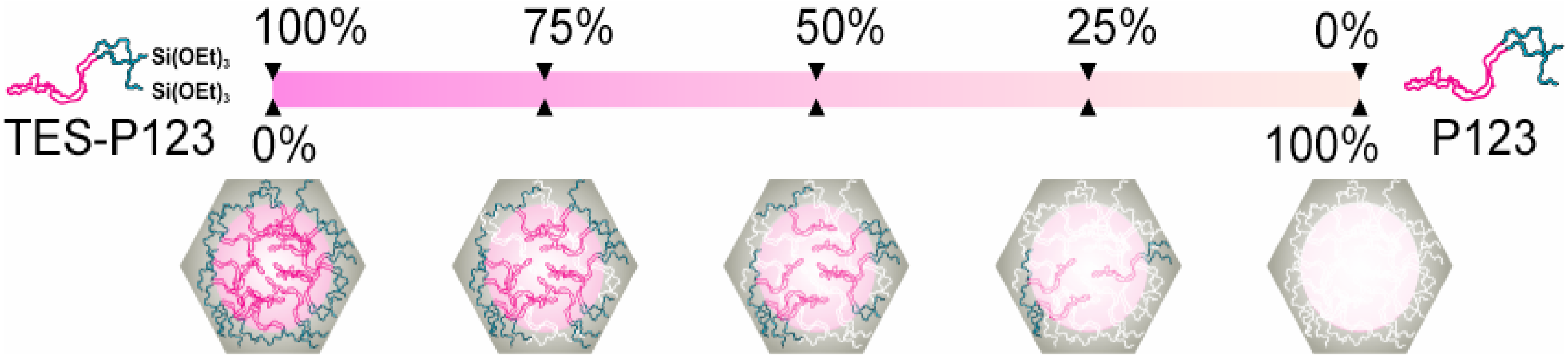
SBA-15 → Large mesopores
Hydrothermal stability

Control of the amount of P123 within mesopores

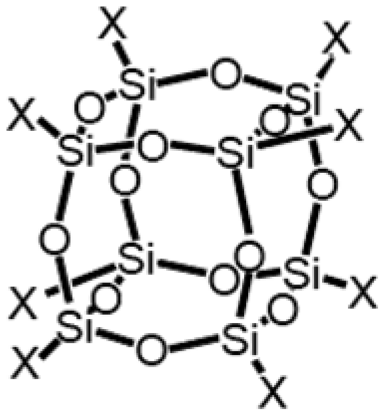


+ TEOS

Selective removal of conventional P123



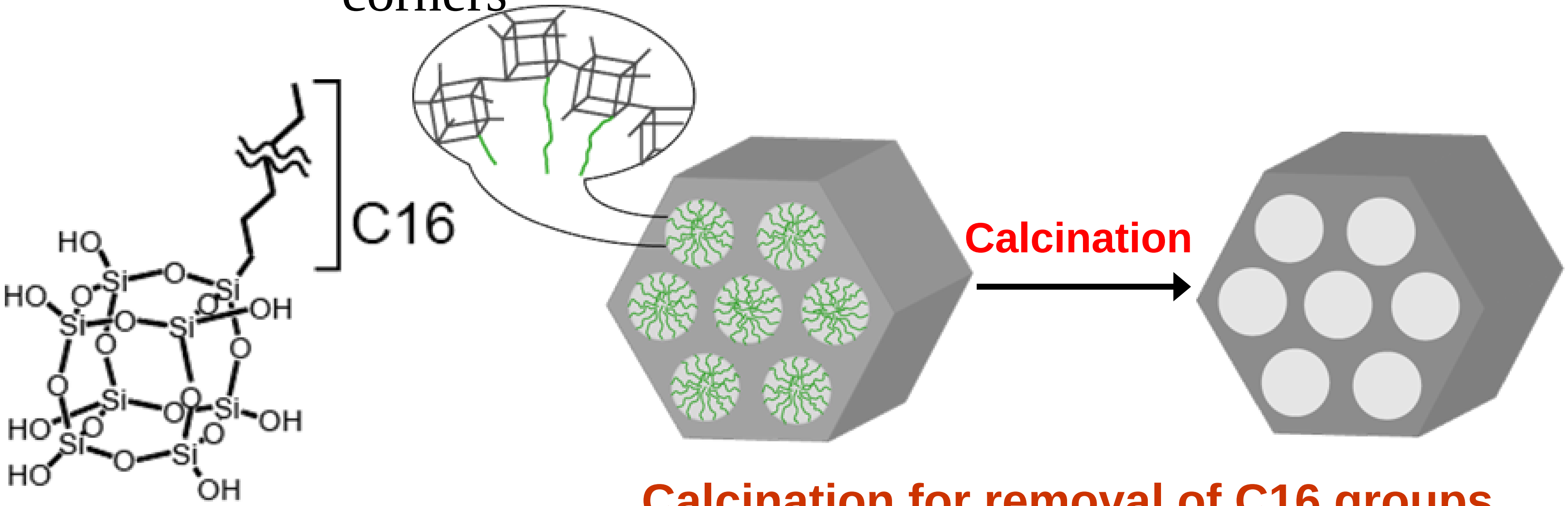
Incorporation of cage-type siloxane units (D4R)units into mesostructured materials



X= -H
-OH
Organic group

D4R units

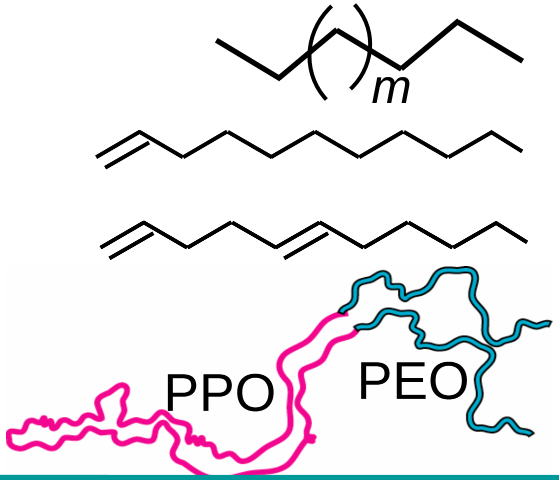
- one of building units for zeolites
- symmetrical
- bonding with various organic groups on the corners



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

Varieties in organosilanes

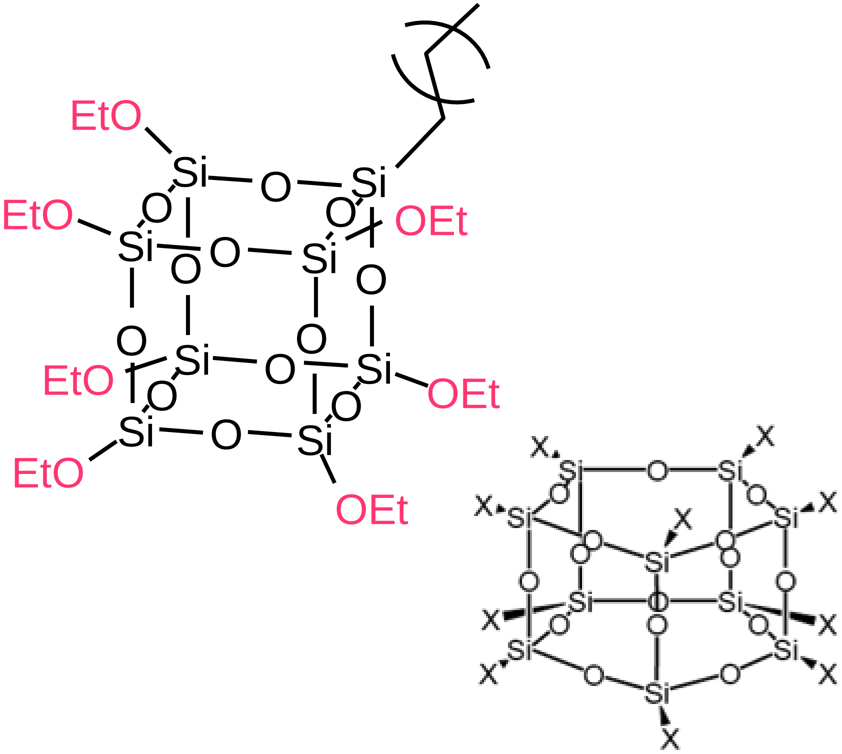
R —— $Si\text{-}X_3$



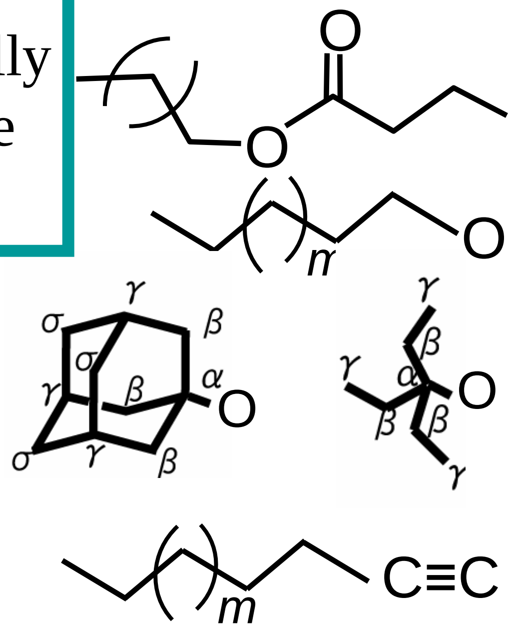
$SiCl_3$

$SiOR_3$

$Si(OSi(OR)_3)_3$



Chemically
Cleavable
Groups



Alkoxychlorosilanes

Alkoxychlorosilanes $(RO)_nSiCl_{4-n}$

Different reactivities of
alkoxy groups and chloro groups

Grafting with chloro groups

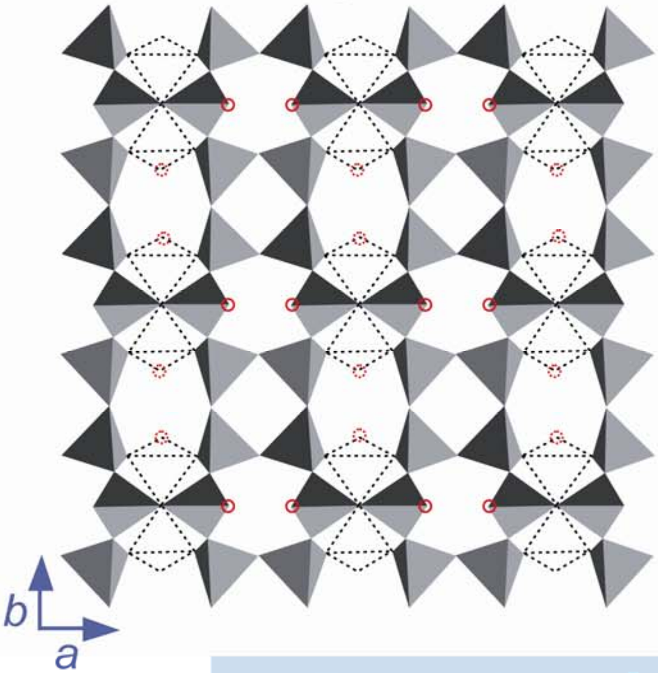
Incorporation of SiO_4 units into(onto) silicates

Soft chemical removal of alkoxy groups by hydrolysis

Silylation of octosilicate

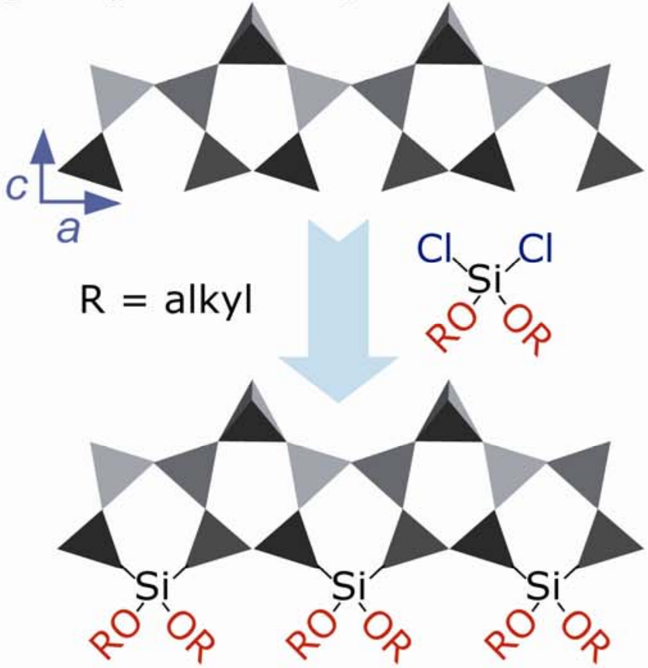
Octosilicate

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



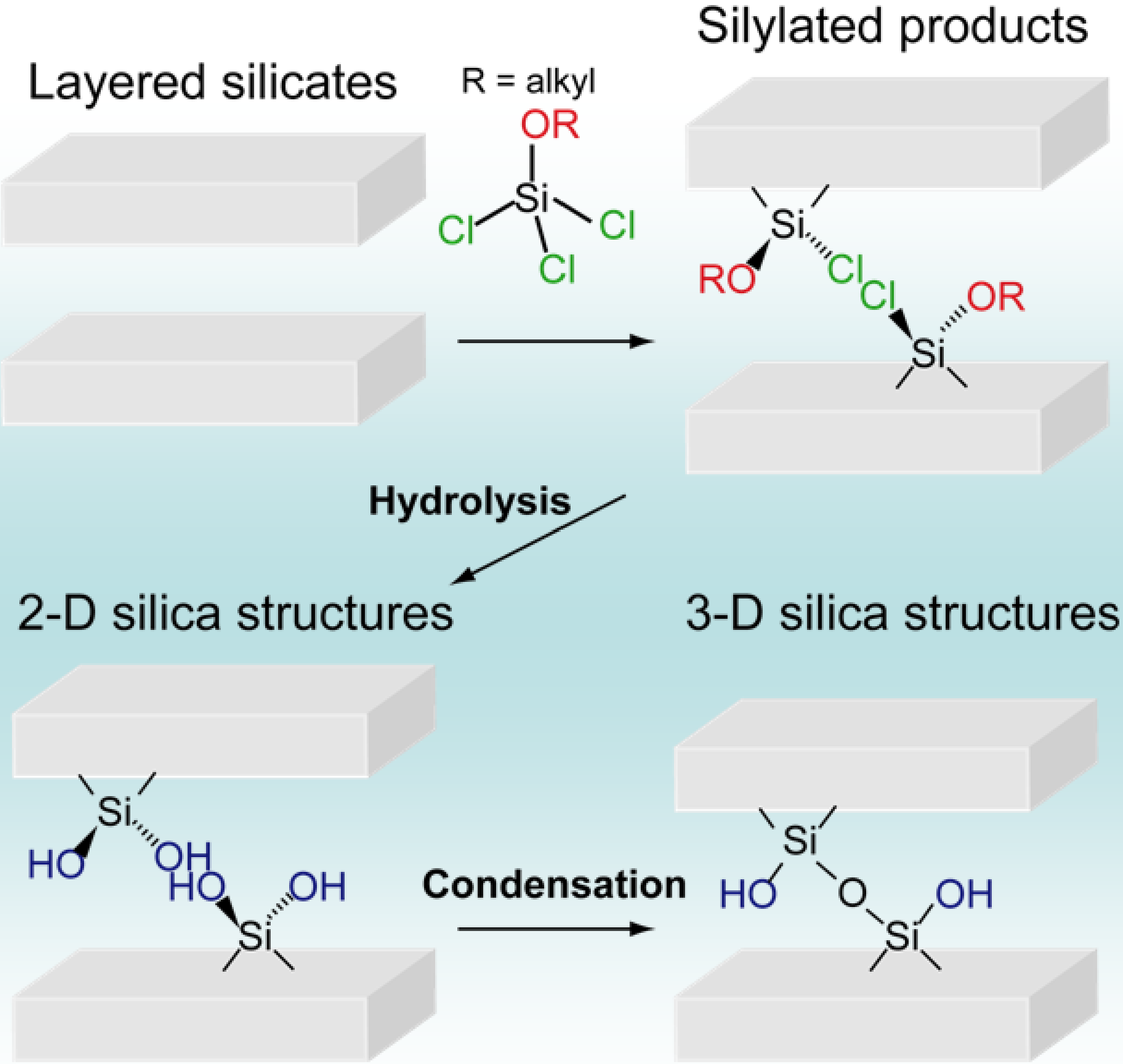
Silylation of Octosilicate with Dialkoxydichlorosilanes

Controlled grafting of dialkoxysilyl groups onto layered silicate



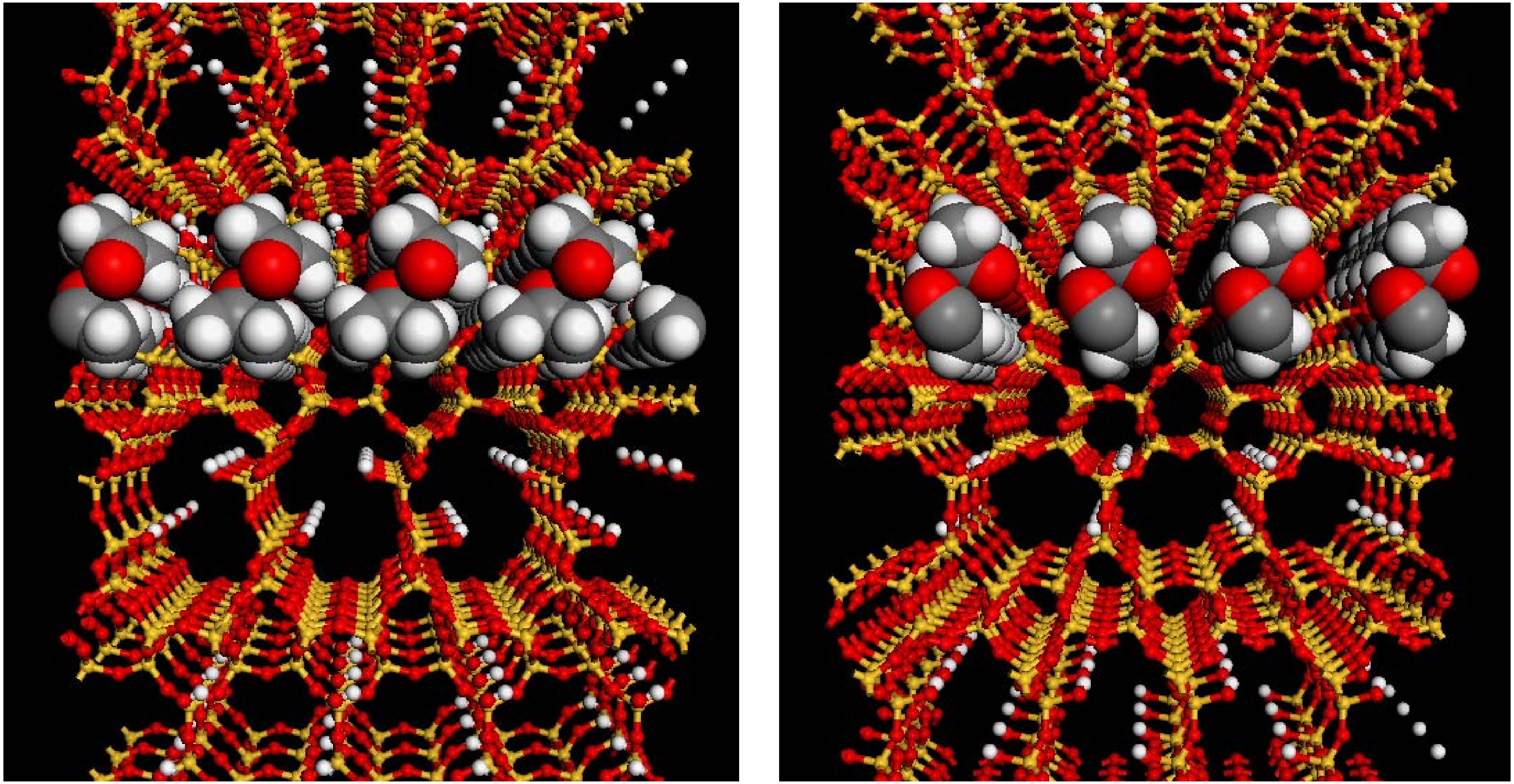
Formation of Novel Molecularly Ordered Alkoxysilylated-Derivatives of Layered Silicate

D. Mochizuki, A. Shimojima, K. Kuroda, *J. Am. Chem. Soc.*, **124**, 12082 (2002)



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

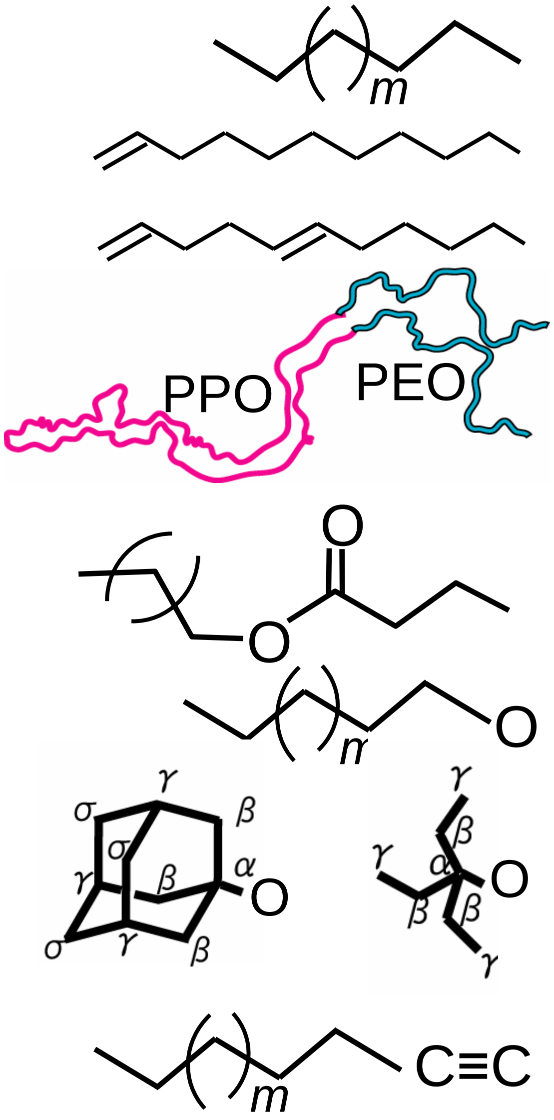
D. Mochizuki, A. Shimojima, K. Kuroda, JACS (2005)



Mochizuki, Shimojima, Kuroda, JACS (2005)

Lots of opportunities in materials chemistry

R —— $Si\text{-}X_3$



$SiCl_3$

$SiOR_3$

$Si(OSi(OR)_3)_3$