Nanoporous Materials:
ordered mesoporous silica, non-oxides, and materials with pore hierarchy

UCSB-ICMR Summer School on 'Preparative Strategies in Solid State and Materials Chemistry'

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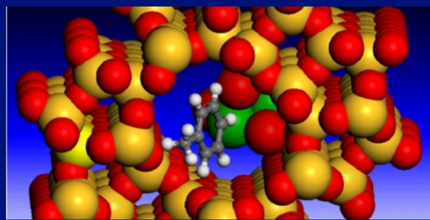
Ryong Ryoo

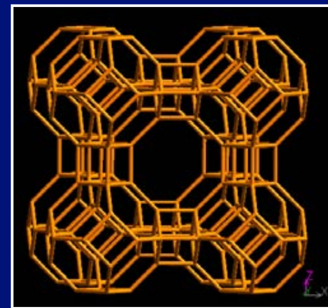
Department of Chemistry, and Graduate School of Nanoscience and Technology (WCU), KAIST, Daejeon 305-701, Korea. E-mail: rryoo@kaist.ac.kr

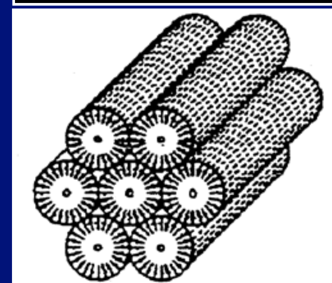
Nanoporous Materials

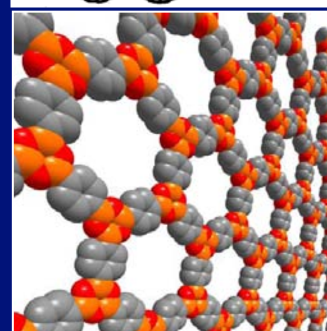


Catalysis
(green chemistry)

Separation
(pollutant removal)







Electrode
(fuel cell, EDLC)

Gas storage
(hydrogen storage)

IUPAC definition of porous structure

microporous | mesoporous | macroporous

2 nm | 50 nm

General Strategy: Use Pore-Generating Agent (Porogen)

-Pore generation in a condensed matter is a thermodynamically unfavorable, non-spontaneous, energy-consuming process.

-Regular pore arrangement is unfavorable because of low entropy as compared to irregular arrangement of pores with different diameters and shapes.

- Many synthetic strategies use pore-generating agent (porogens): single molecule, metal ion, organic ammonium ion, supramolecular assembly of molecules, or pre-made hard template.

Lecture Contents

General Routes to Ordered Mesoporous Materials

Ordered Mesoporous Carbons

Mesoporous Organic Polymers

Mesoporous Metal Chalcogenides

Hierachically Porous Systems

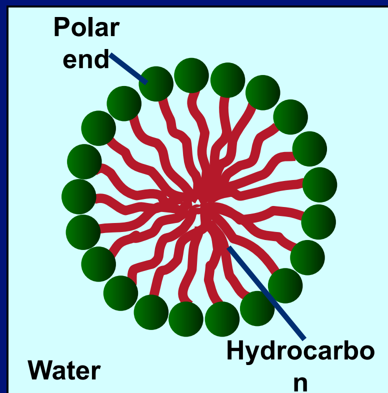
General introduction

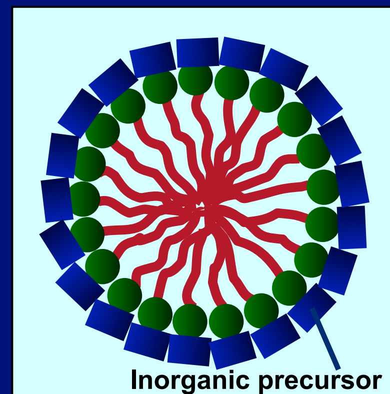
Hierarchically porous zeolites:

"Synthesis of Nanostructured Zeolitic Architectures Assembled by Zeolite-Structure-Directing Surfactants"

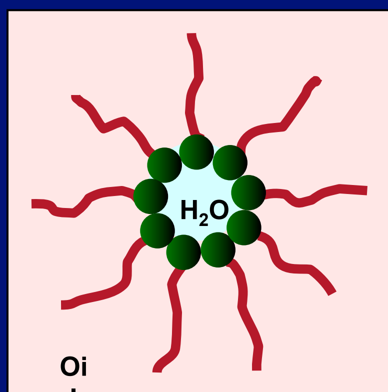
Cooperative Assembly Mechanism between Organic Surfactant and Material Precursors, Leading to Mesostructured Materials

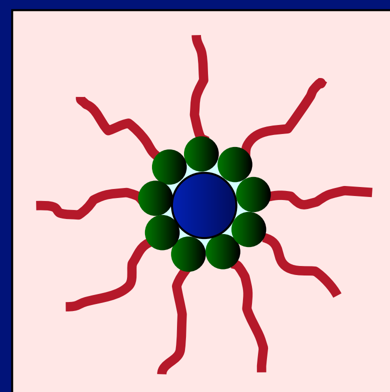
Micelle





Inverse Micelle



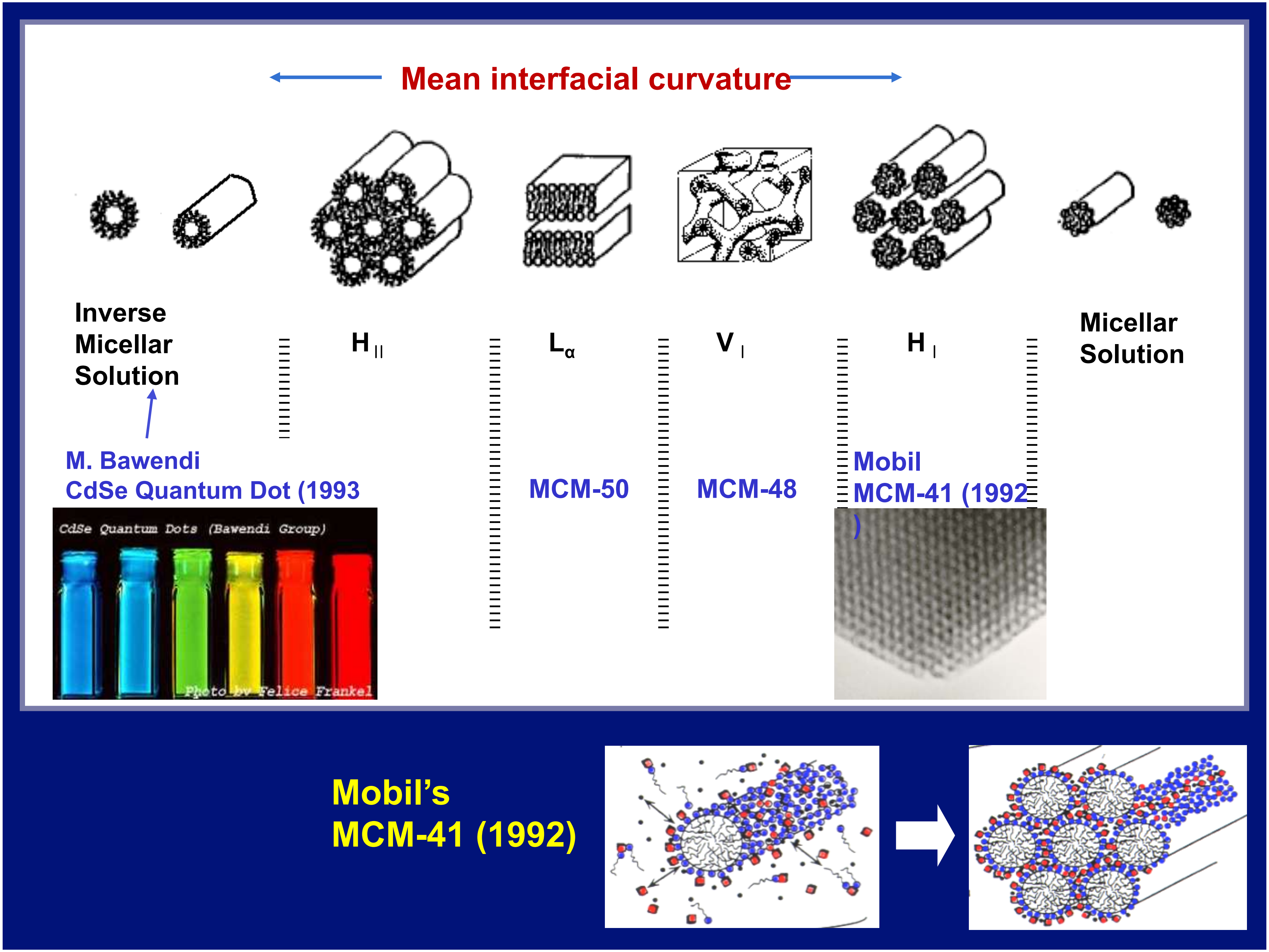


$CH_3(CH_2)_nN^+(CH_3)_3\ Br^-$
Cationic Surfactants

$CH_3(CH_2)_nCOO^-\ Na^+$
Anionic Surfactants

$H(OCH_2CH_2)_n\ (OCH(CH_3)CH_2)_m\ (OCH_2CH_2)_nOH$
Nonionic Surfactants

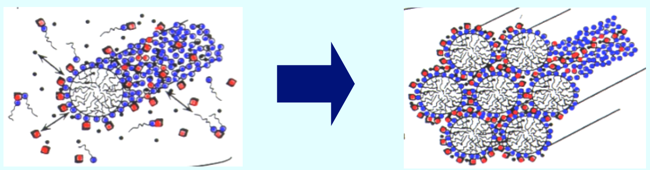
Organic surfactants form inorganic-organic composite micelles via cooperative assembly with inorganic precursors. This is often referred to as 'Supramolecular Templating Process of Surfactants for Nano-Structured Inorganic Materials', or 'Soft Templating' Route.



Mean interfacial curvature
Inverse Micellar Solution
H_{II}
L_α
V_I
H_I
Micellar Solution
M. Bawendi
CdSe Quantum Dot (1993
CdSe Quantum Dots (Bawendi Group)
Photo by Felice Frankel
MCM-50
MCM-48
Mobil
MCM-41 (1992
)
Mobil's
MCM-41 (1992)

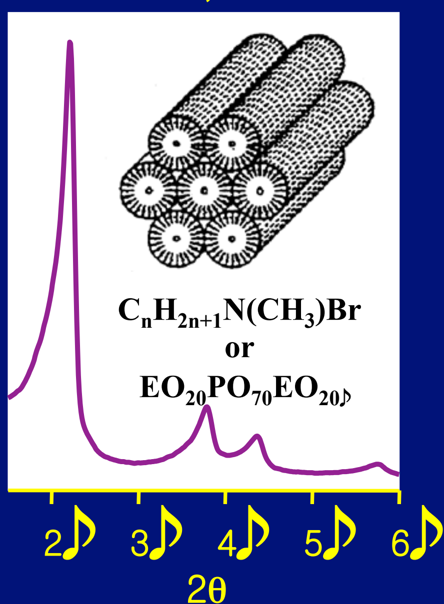
Ordered Mesoporous Silica with Various Structures

Synthesis Conditions
- Tetraethylorthosilicate, Na-silicates
- Acidic, basic, neutral conditions
- Cationic, non-ionic, anionic surfactants

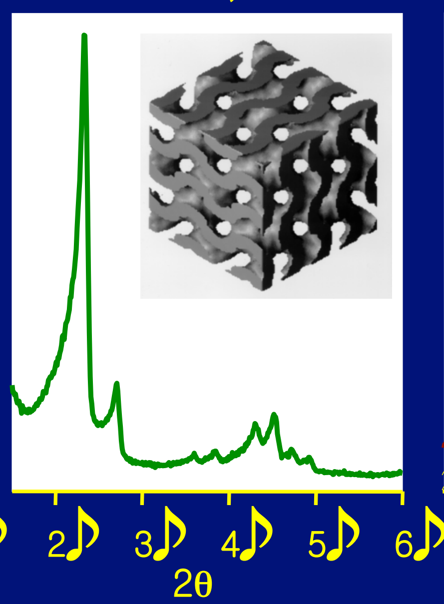


− Easily removable templates
- Various channel structures
- Controllable pore sizes between 2-20 nm

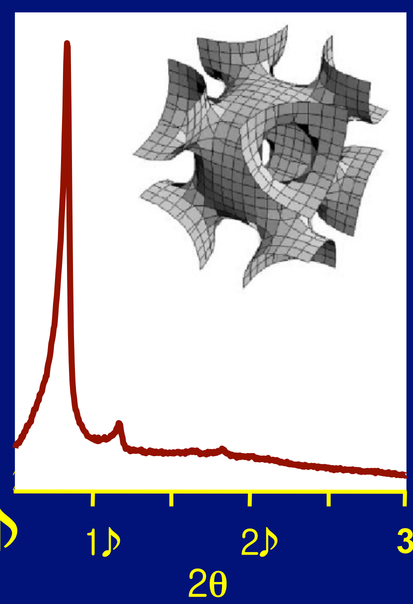
Hexagonal *p6mm*
MCM-41, SBA-15



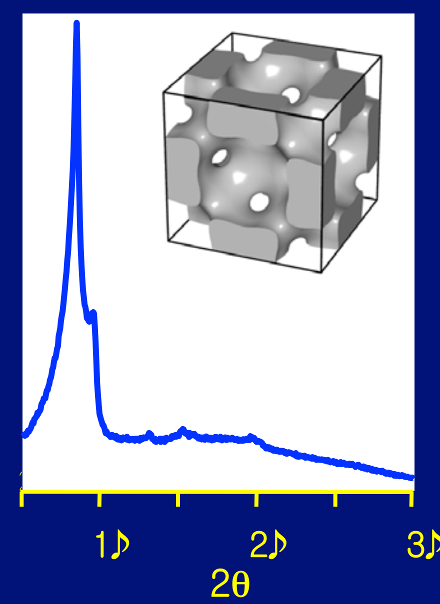
Cubic *Ia$\bar{3}$d*
MCM-48, KIT-6



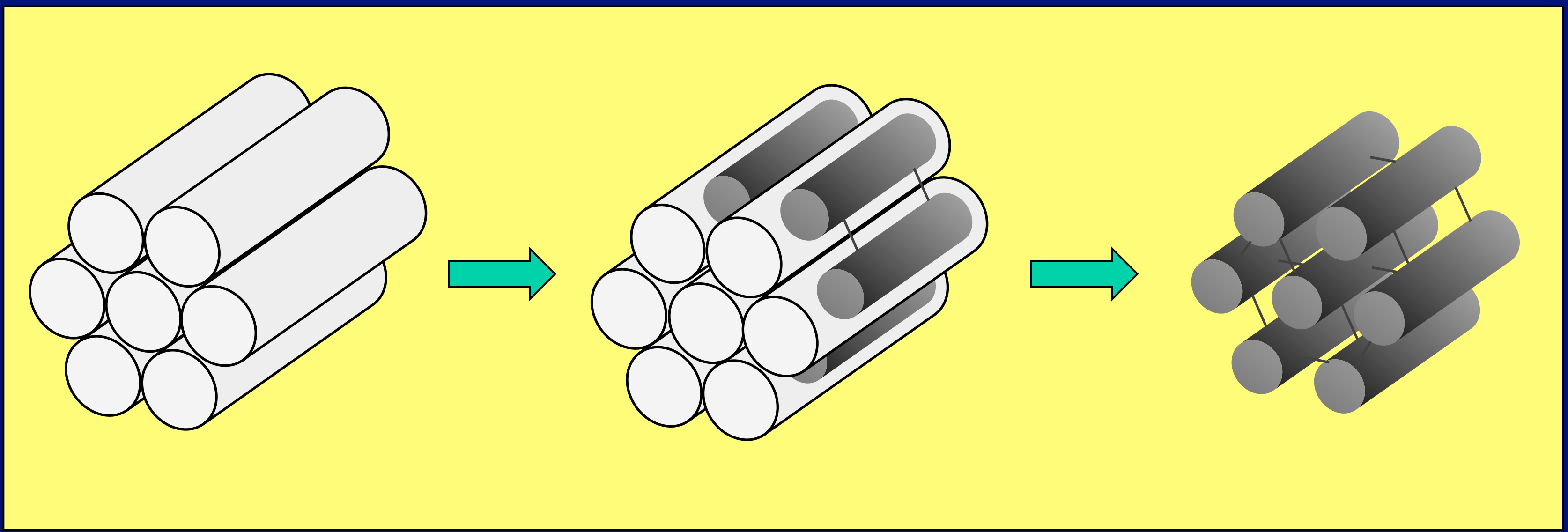
Cubic *Im$\bar{3}$m*
SBA-16



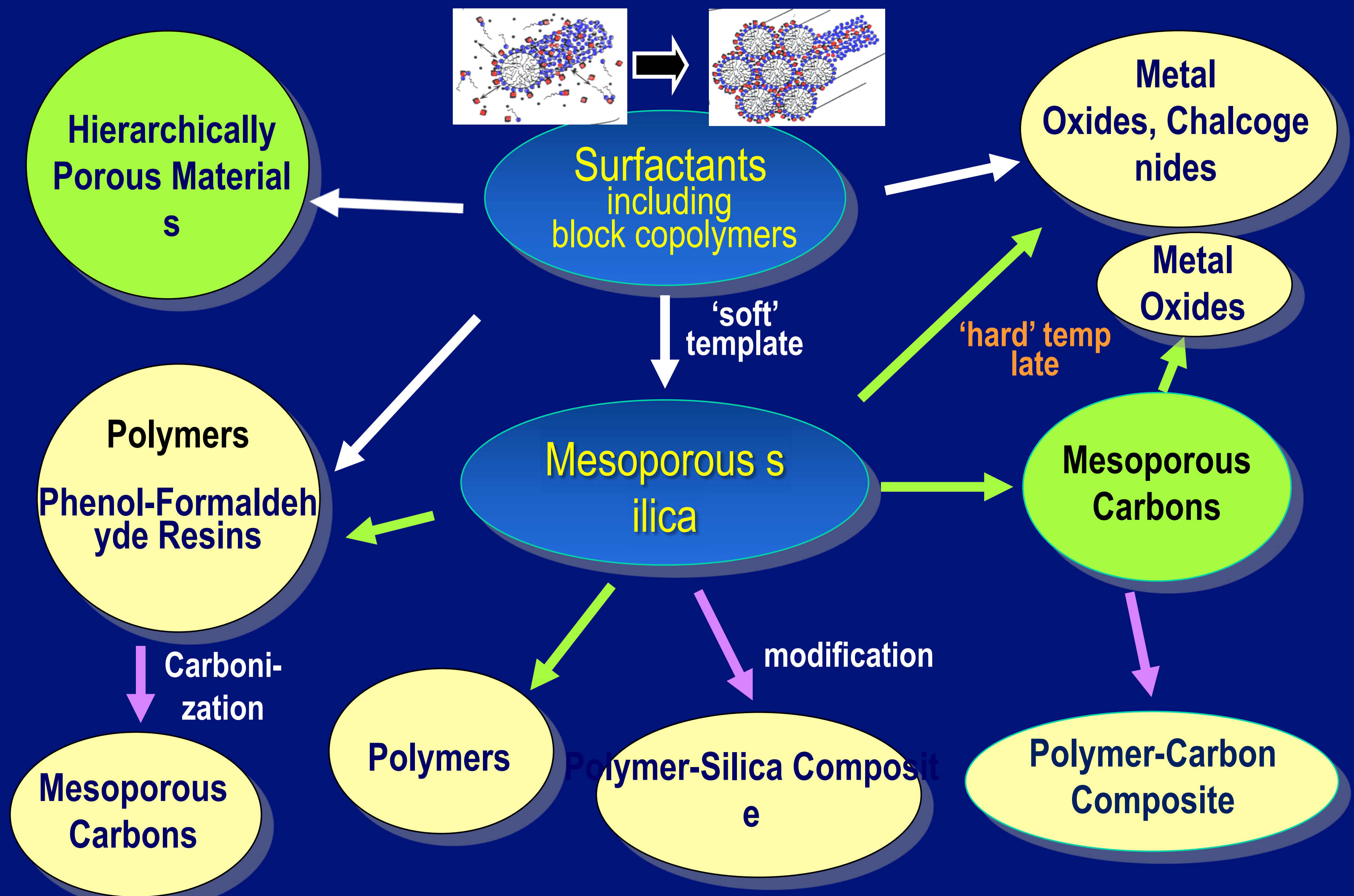
Cubic *Fm3m*
KIT-5



‘Hard Templating’ Route to Other Mesostructured Materials Using Mesoporous Silica

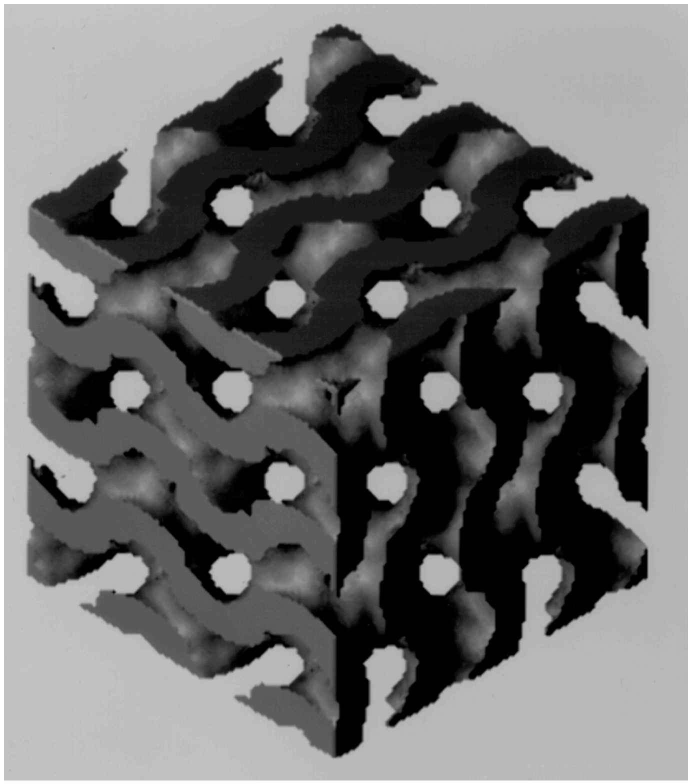


Various Materials Available via Surfactant-Assembling Route and Hard-Templating Route



Ordered Mesoporous Carbon

Synthesis of Carbon Using Mesoporous Silica Template



Mesoporous Silica MCM-48♪

Sucrose/ Mesoporous Silica

↓ H_2SO_4 catalyst, pyrolysis

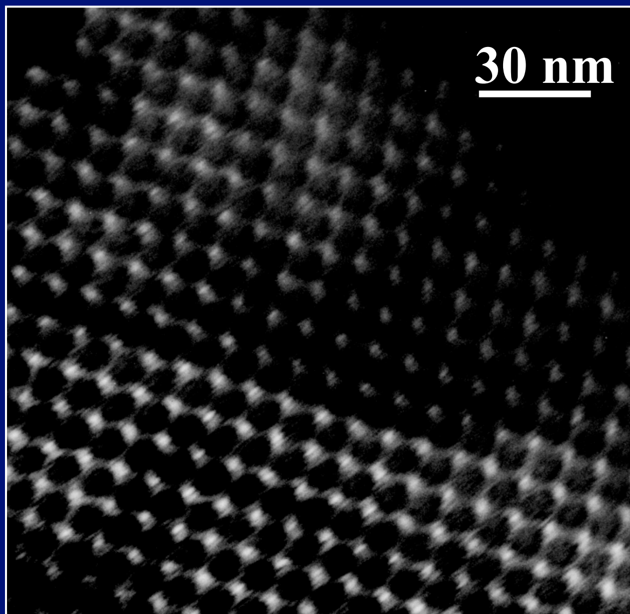
Carbon/ Mesoporous Silica

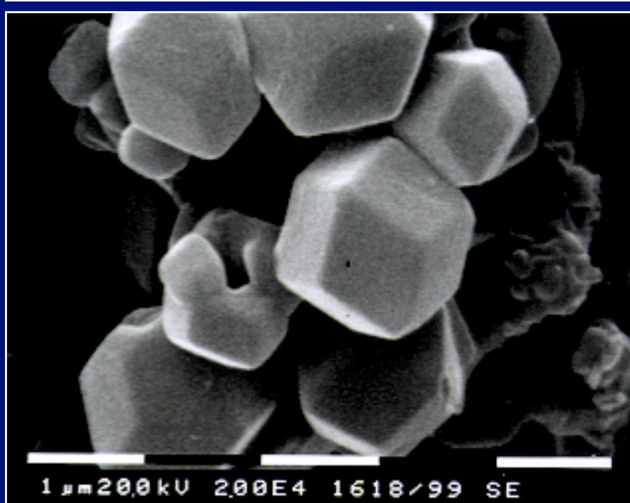
↓ NaOH or HF solution

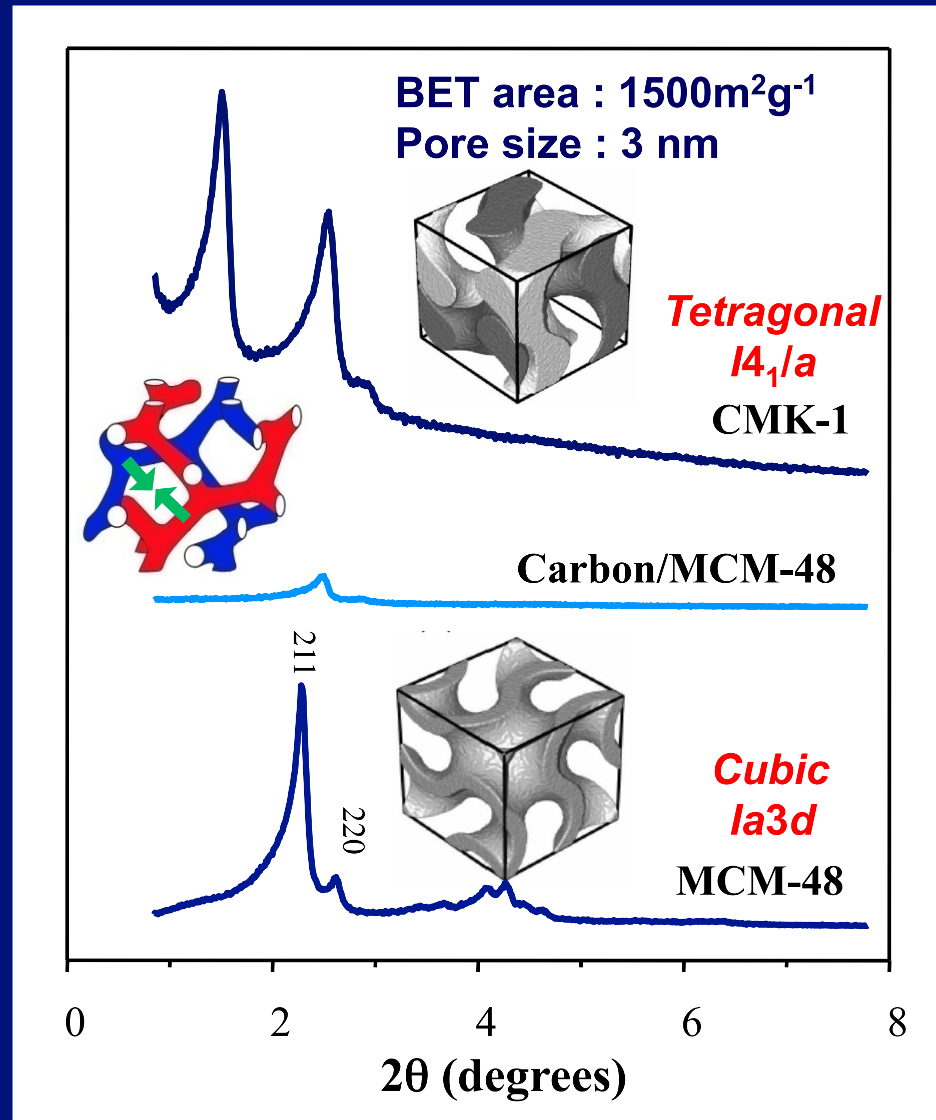
Mesoporous Carbon

(R. Ryoo et al., *J. Phys. Chem. B*, 1999, *103*, 7743.)

Mesoporous Carbon CMK-1

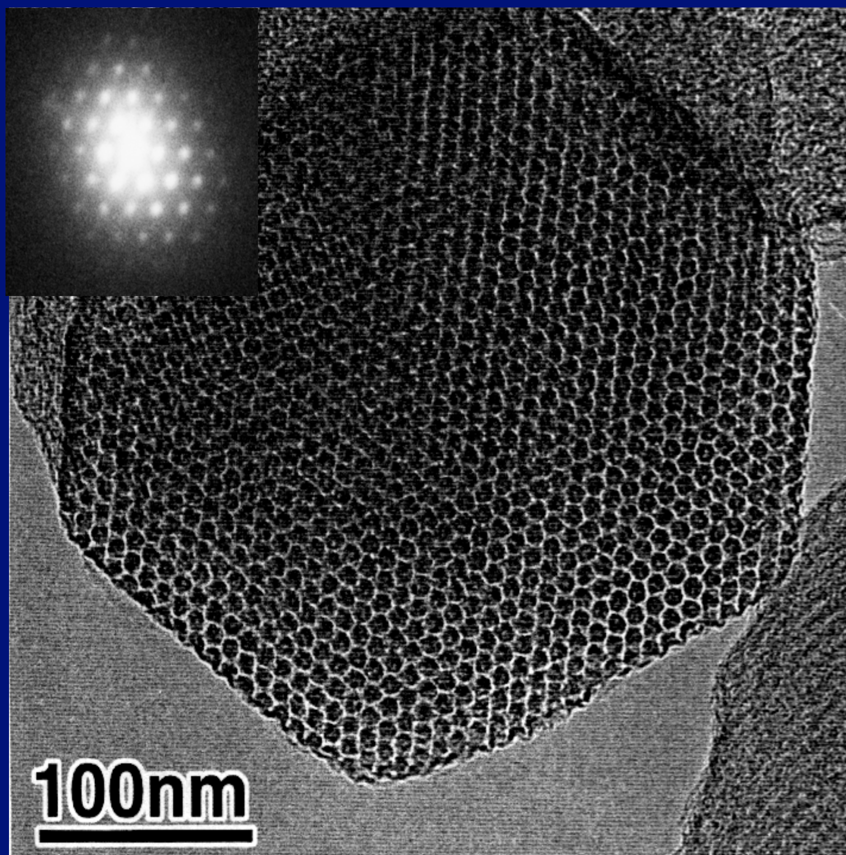


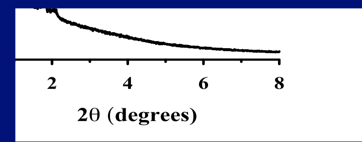


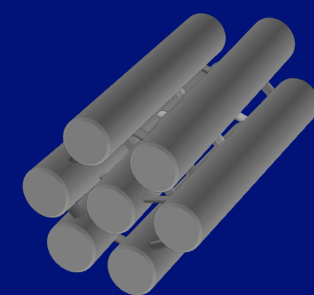


CMK: 'Carbon Mesostructured by KAIST'

Mesoporous Carbon CMK-3

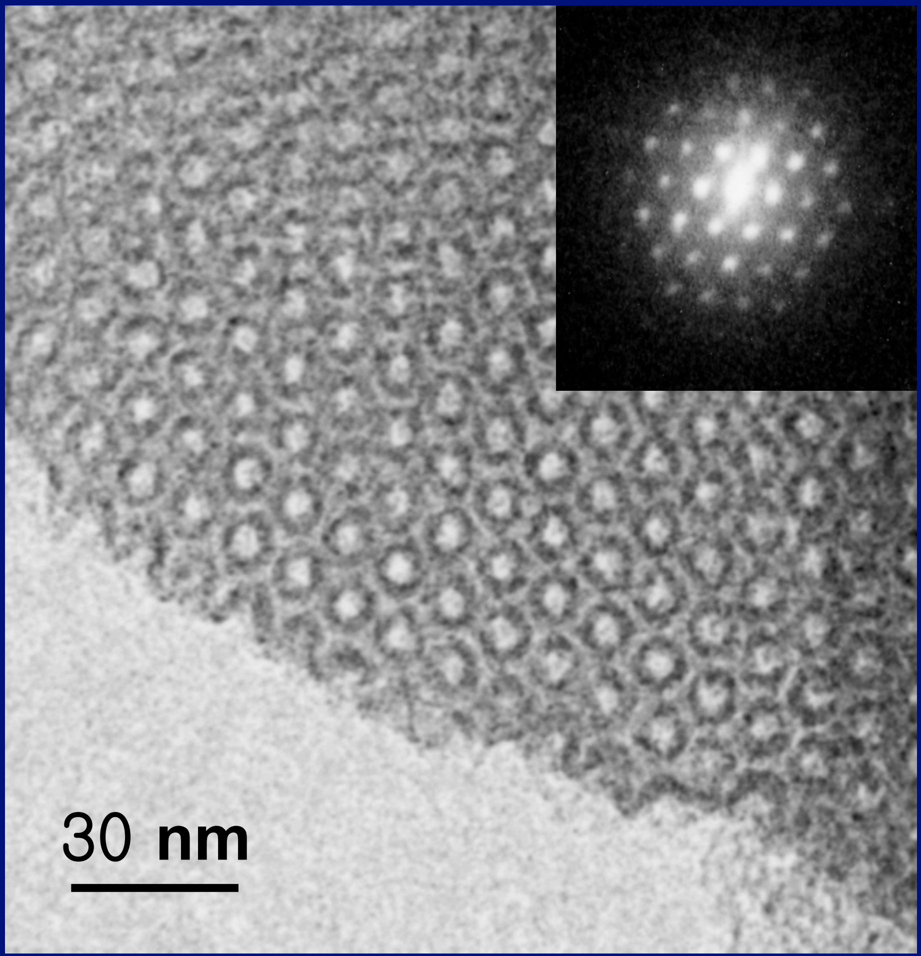


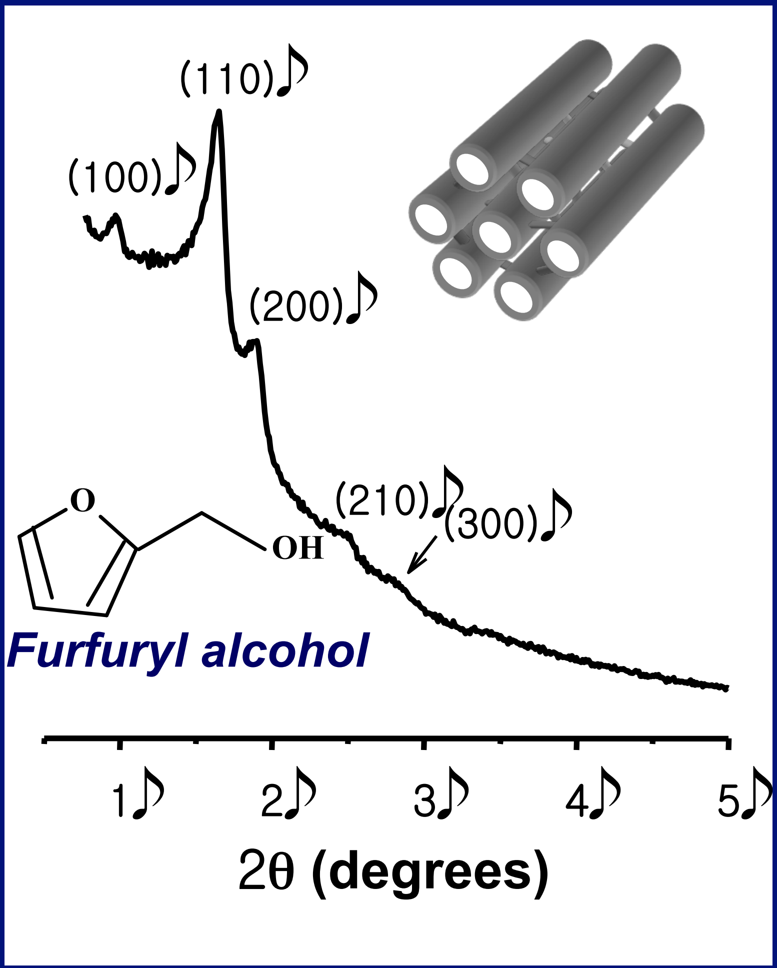




(S. Jun *et al*., *JACS* 2000, *122*, 10712)

Mesoporous Carbon CMK-5



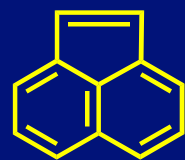


(S. H. Joo *et al.*, *Nature* 2001, *412*, 169)

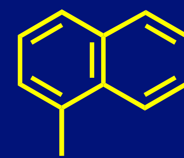
Mesoporous Carbon CMK-3G with Graphitic Frameworks

Using aromatic hydrocarbon sources

Acenaphthene

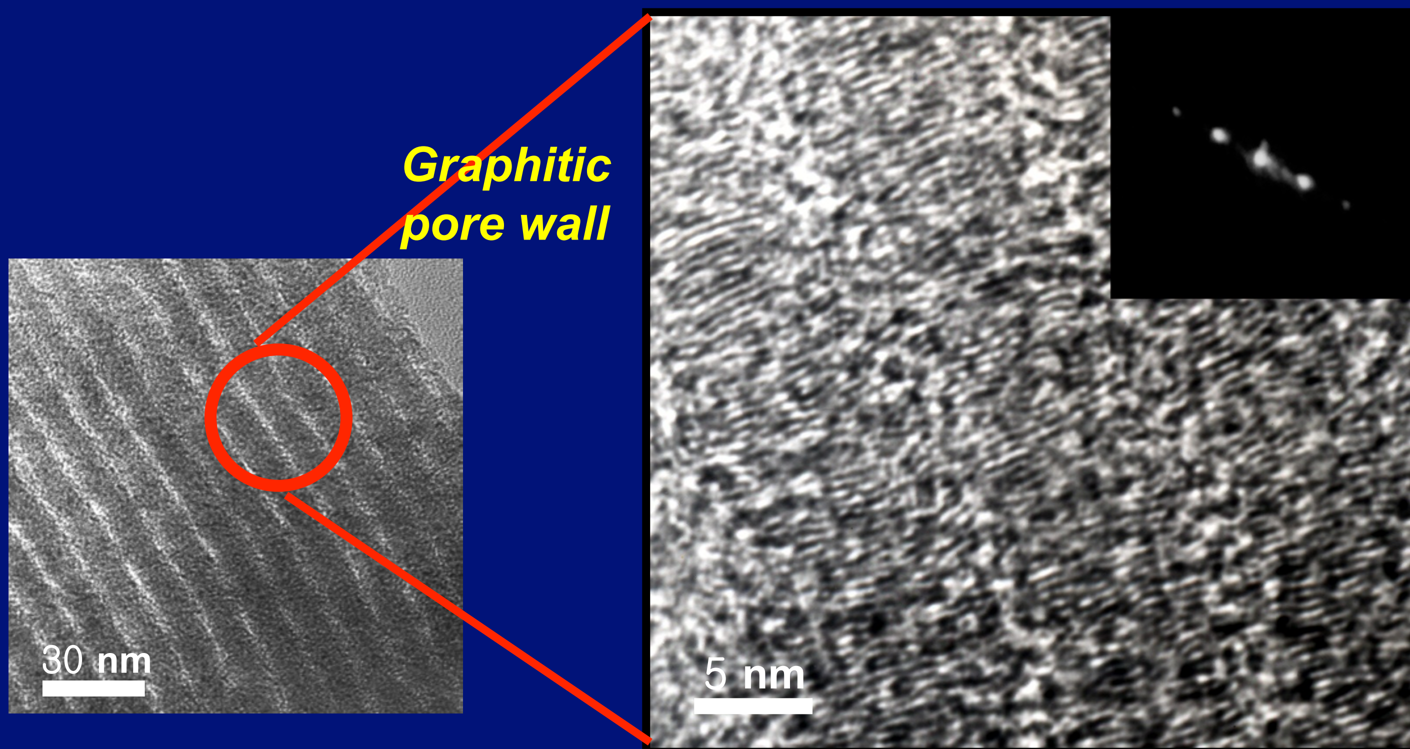


Acenaphthylene



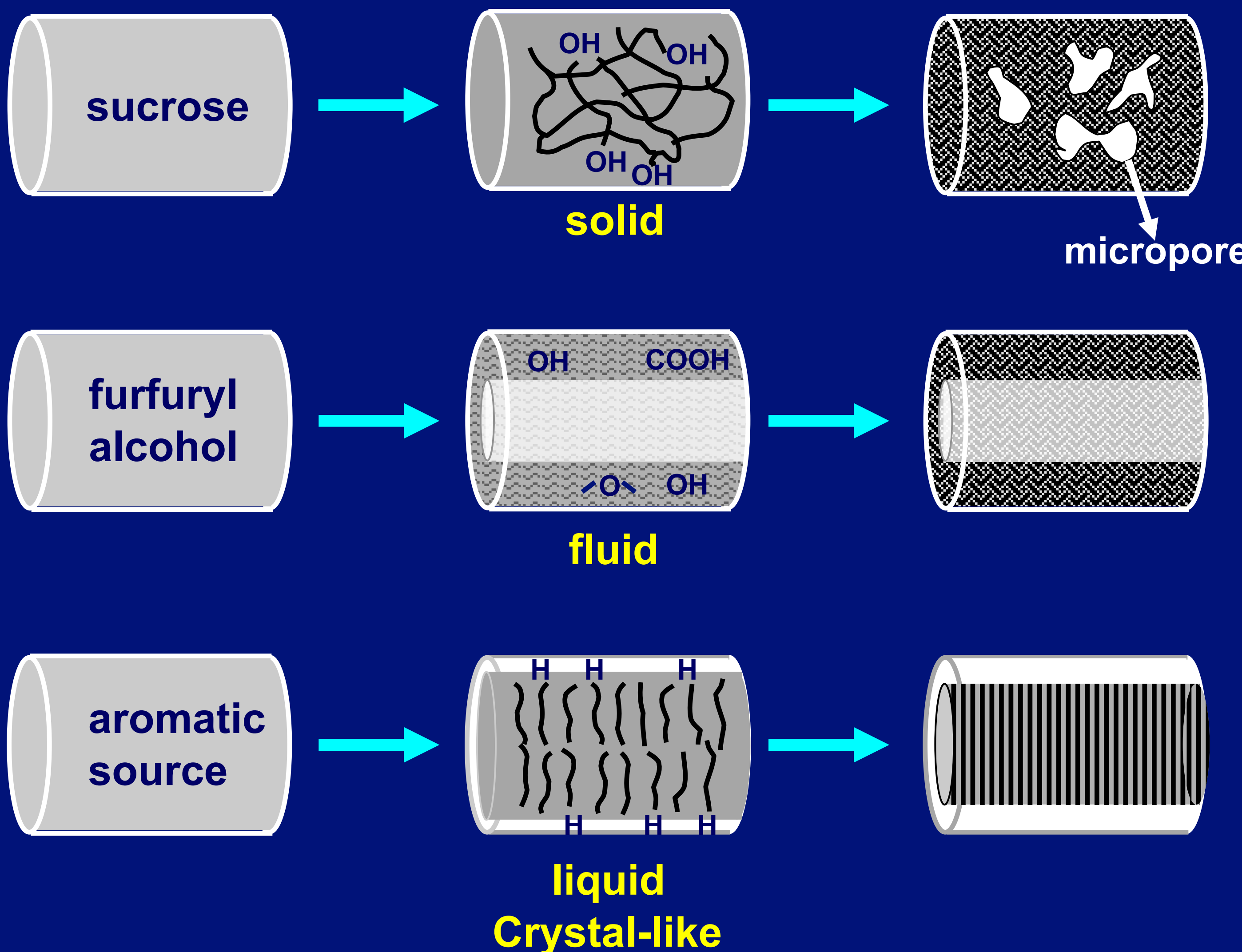
Naphthalene derivatives

Mesophase pitch

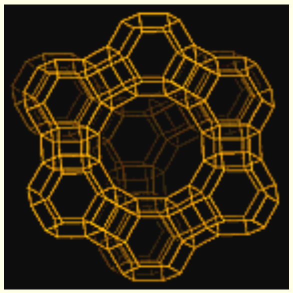


(T.-W. Kim et al., *Angew. Chem. Int. Ed.* 2003, *42*, 4375)

Carbonization Process inside Silica Mesopores

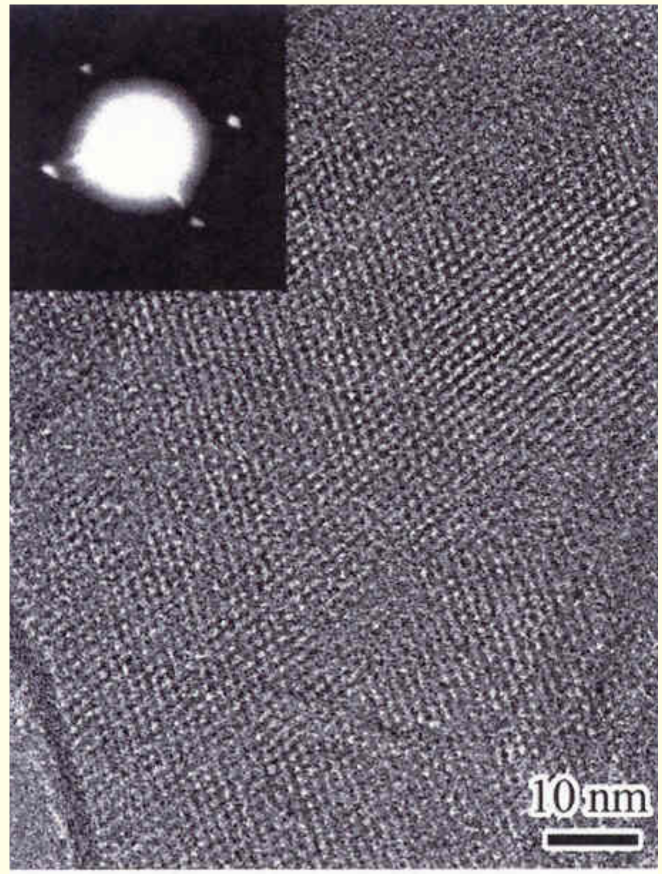


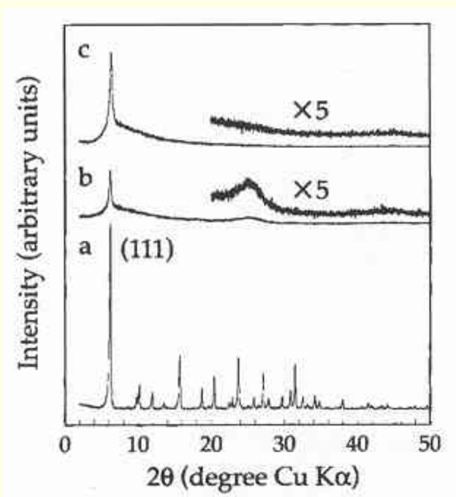
Microporous Carbon Synthesis Using Zeolite Template



Zeolite Y

Carbon rep lication



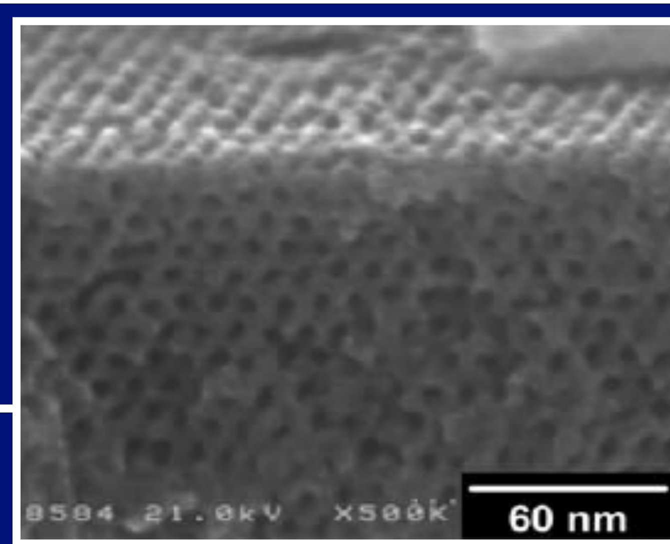


Carbon

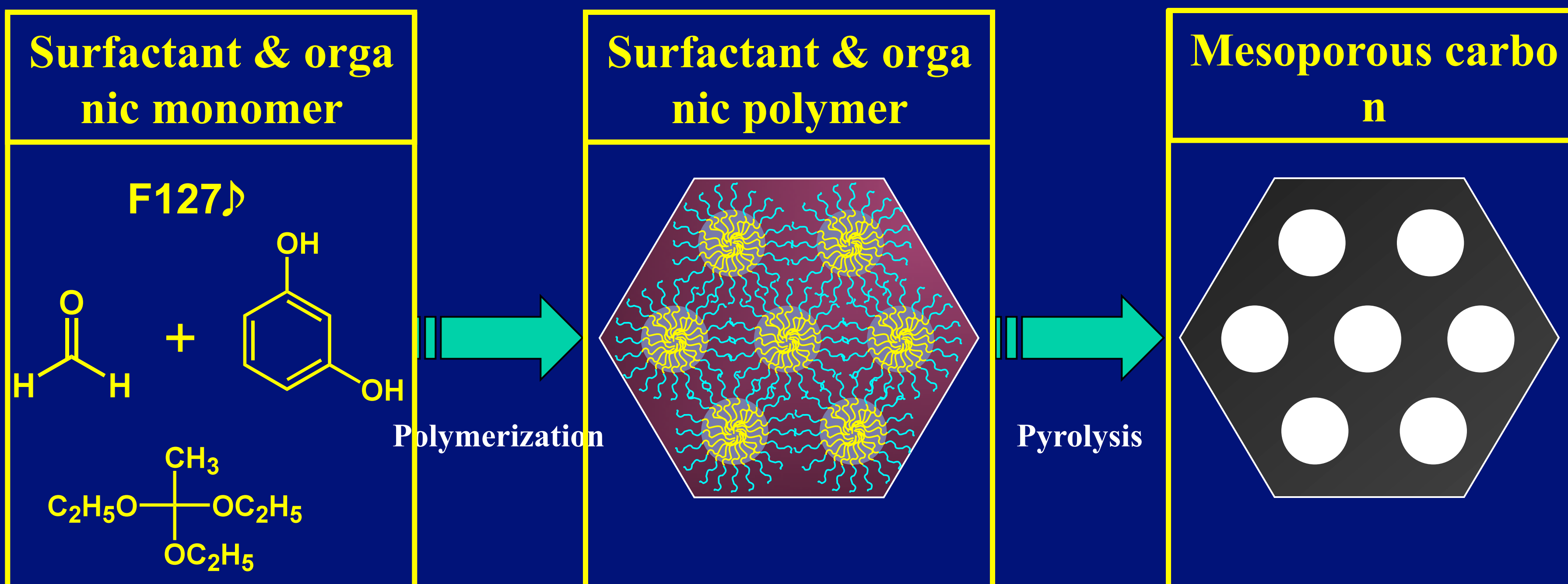
Zeolite Y

(T. Kyotani *et al*., *Chem. Commun.* 2000, 2365; *Chem. Mater.* 2001, *13*, 4413)

Direct Synthesis of Ordered Mesoporous Carbons Using Liquid-Crystal Templating

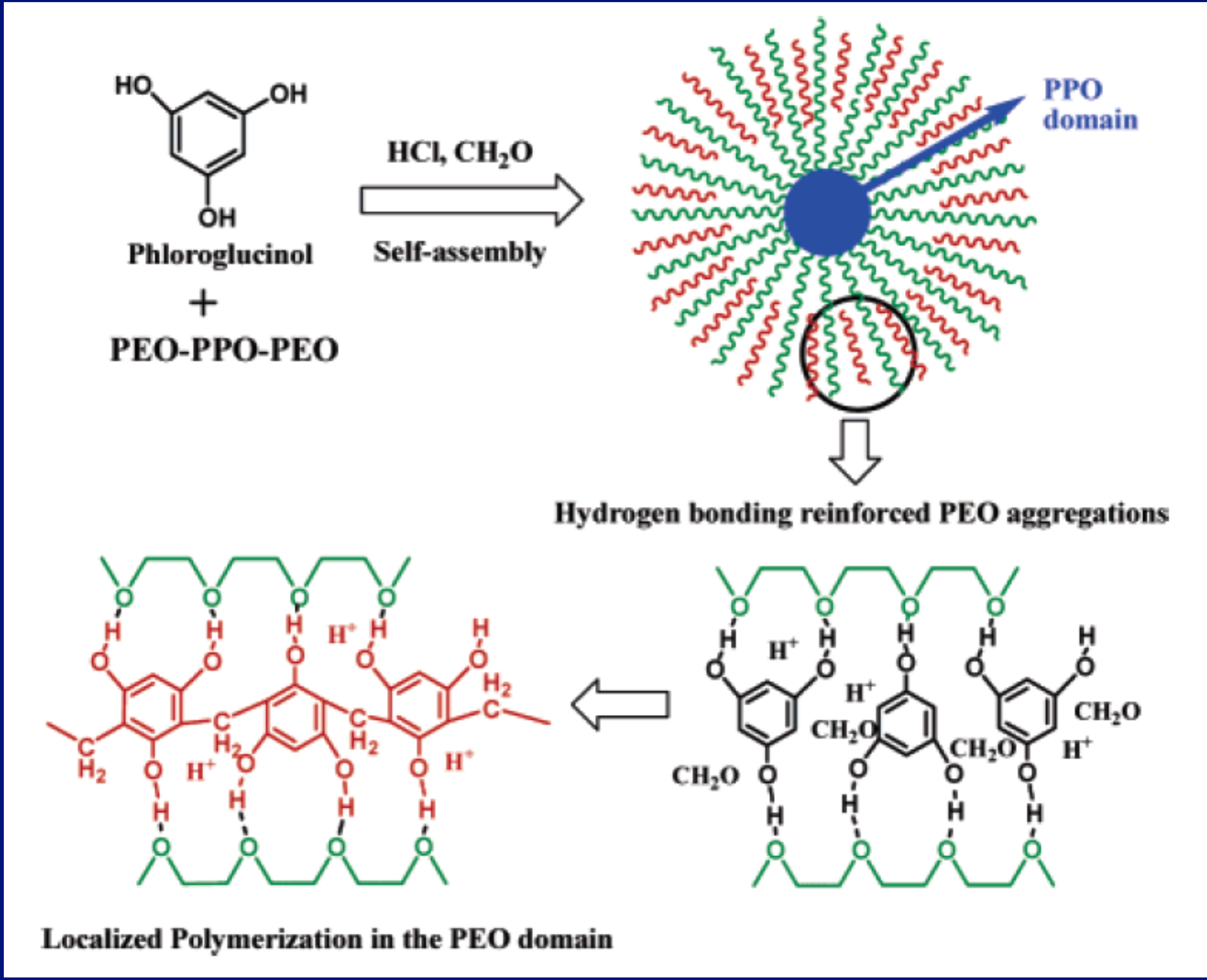


- S. Tanaka *et. al*., *Chem. Commun.* 2005, 2125



- D. Zhao *et. al*. used phenol, F127 and formaldehyde (*Angew. Chem. Int. Ed.* 2005, *44*, *7053*)

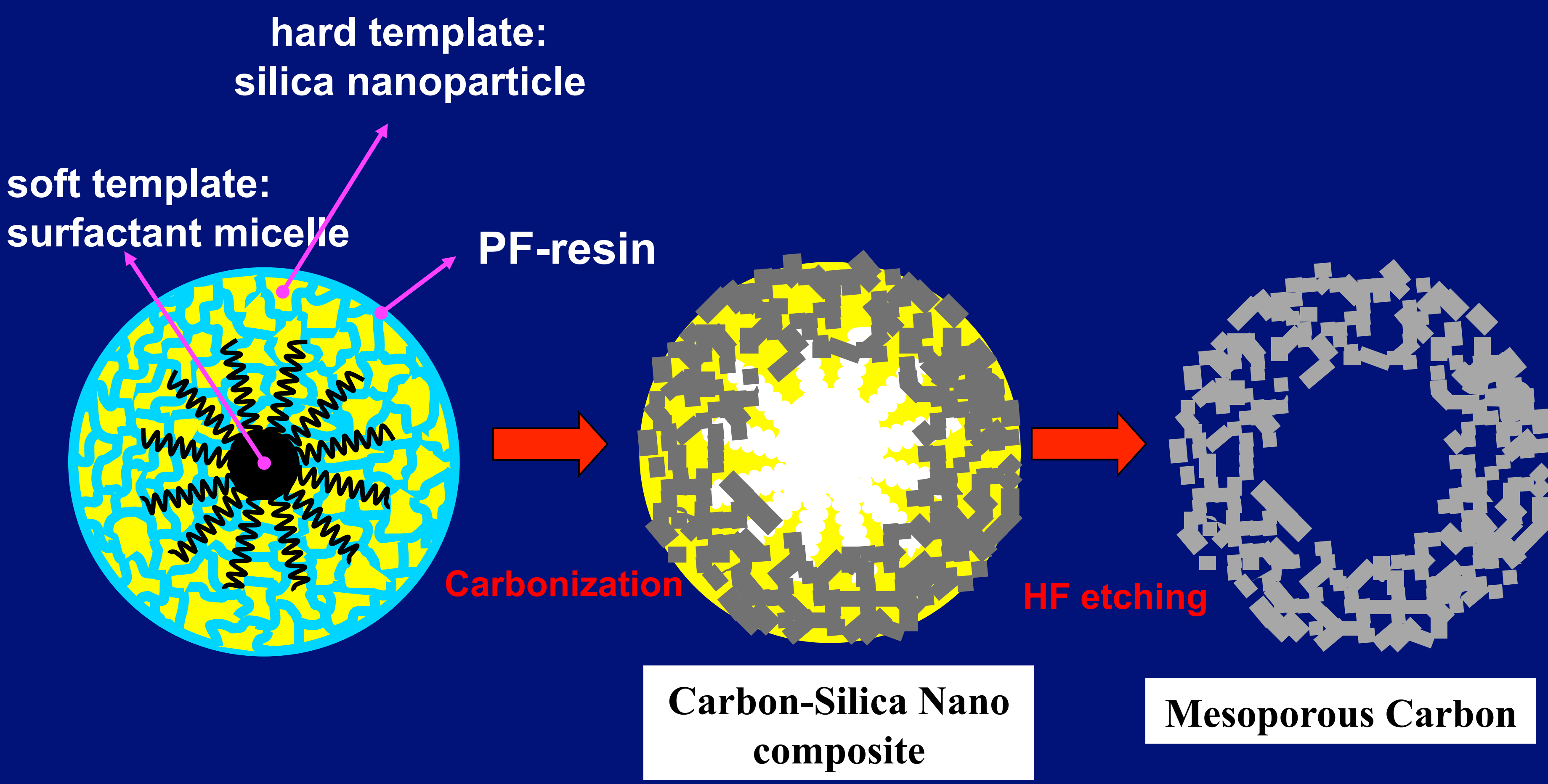
- S. Dai *et. al*. filed the patent earlier, then published in *J. Am. Chem. Soc.* 2006, *128*, 5316



Tri-Constituent Co-assembly to Ordered Mesoporous Carbons

Combination of Soft- & Hard-Templating

(D. Zhao *et. al.*, *J. Am. Chem. Soc.* 2006, *128*, 11660)



Small metal nanoparticles can be supported on ordered mesoporous carbons with high metal dispersion, due to uniform pore environments

Impregnate acetone solutions of metal precursors (H_2PtCl_6, H_2PdCl_4, $RuCl_3$)

↓

Drying at 333 K

↓

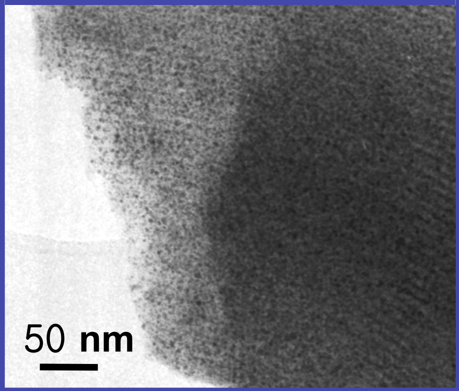
Reduction in H_2 flow at 573 K for 2 h

Highly Dispersed Pt Nanoparticles Supported on Mesoporous Carbon

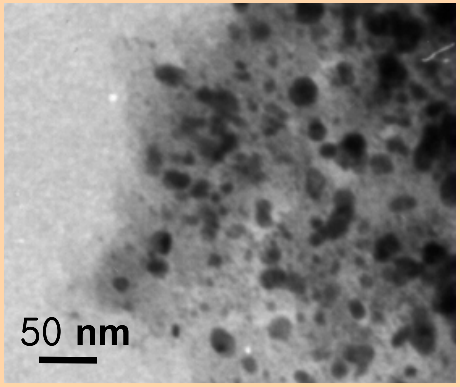
(S. H. Joo et al., *Nature* 2001, *412*, 169)

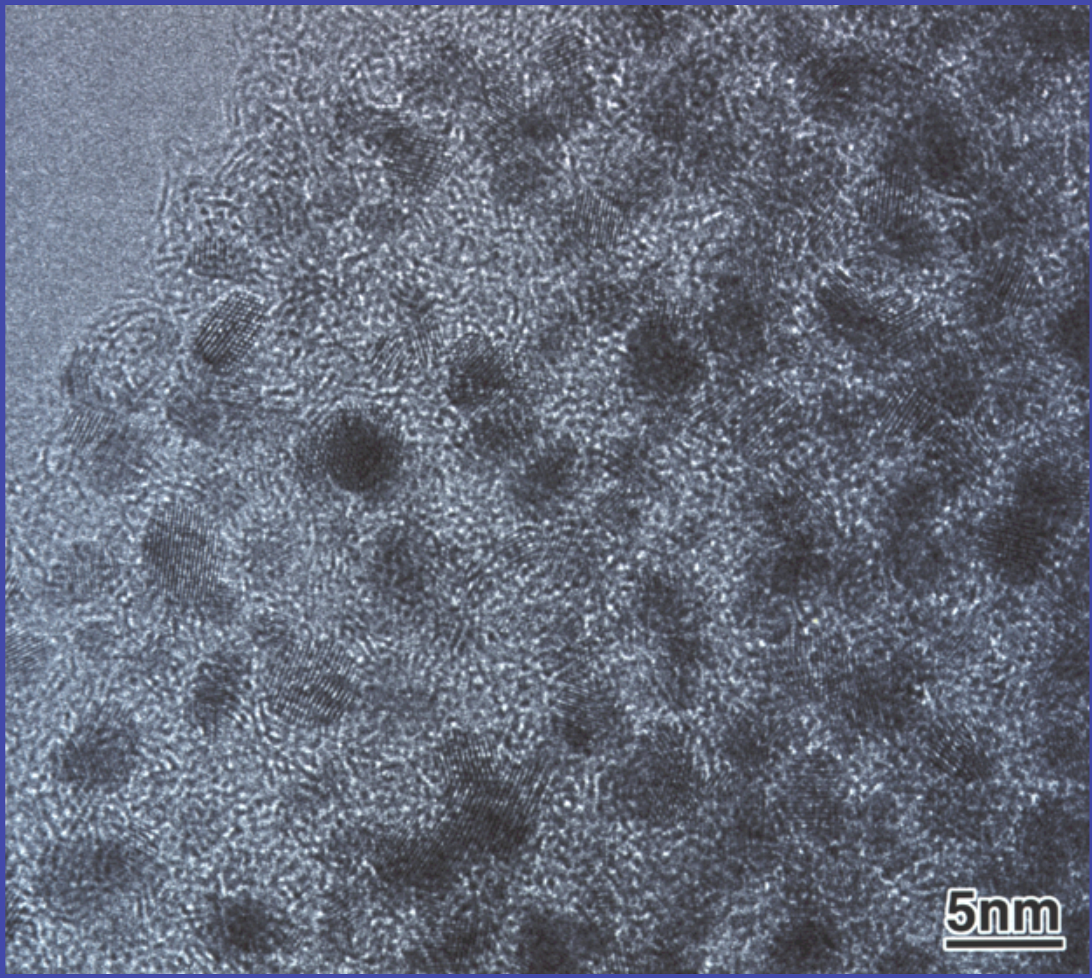
Pt particle size around 2.5 nm even the Pt loading increased up to 50%

Pt/carbon nanopipe



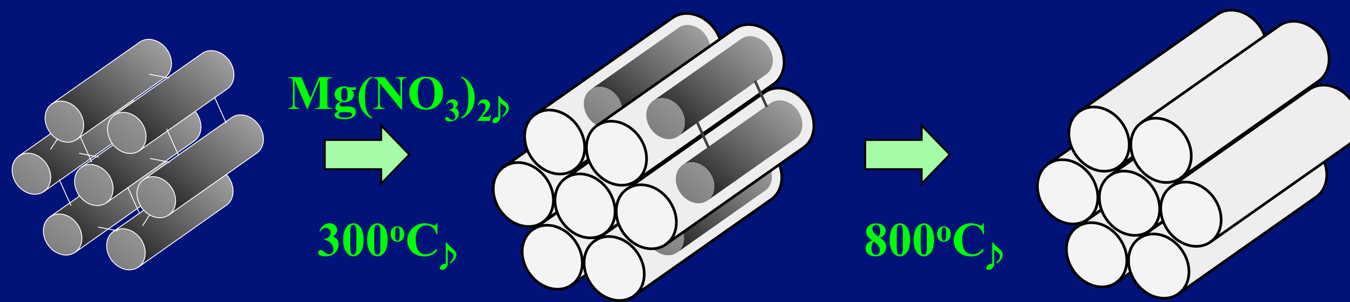
Pt/carbon black



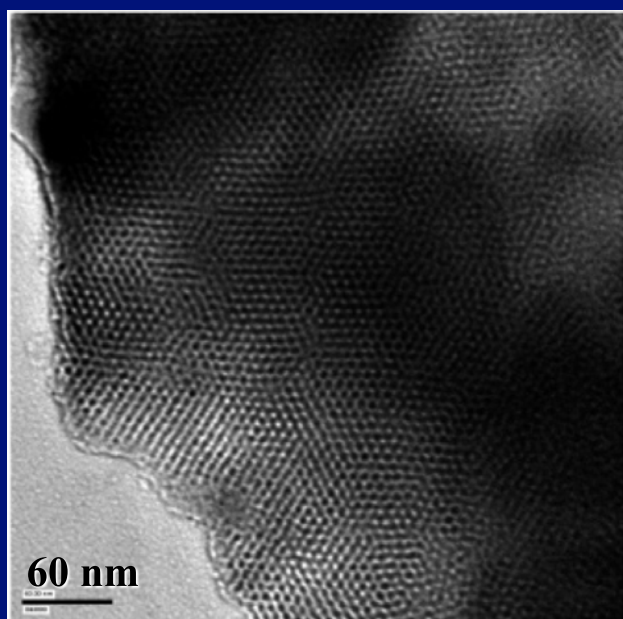


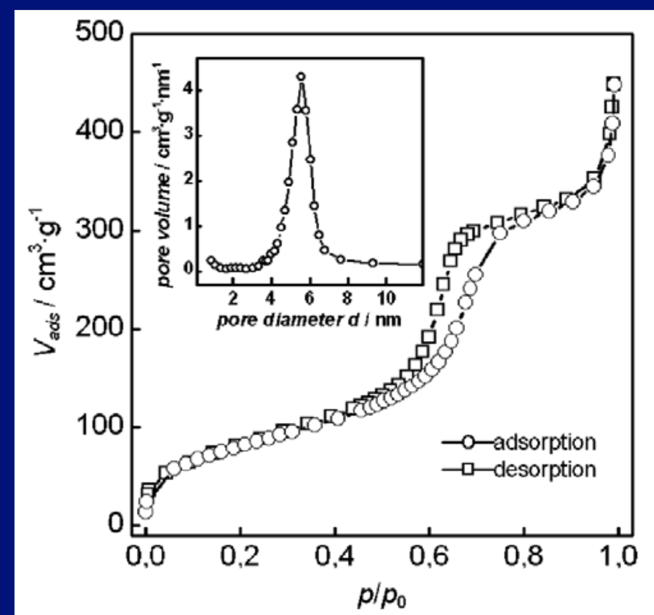
High dispersion is the advantage of the uniform pore environment !

Fabrication of Ordered Mesoporous MgO with High Thermal S tability, Using CMK-3 Carbon Template



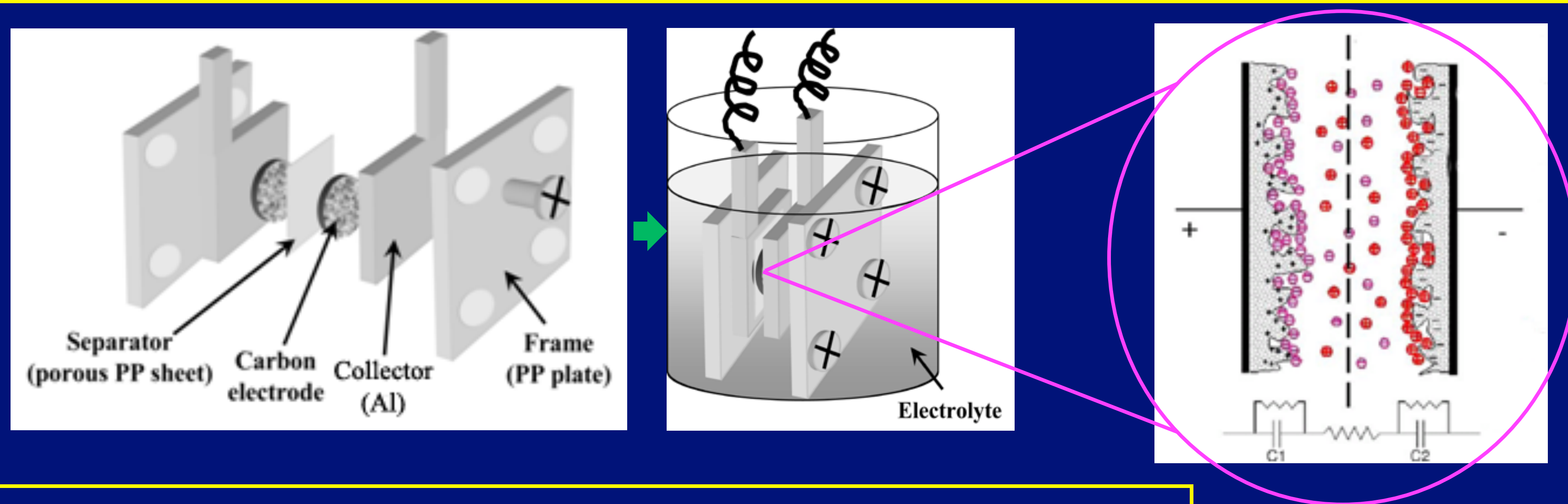
Mesoporous car bon **MgO/carbon** **Mesoporous Mg O**



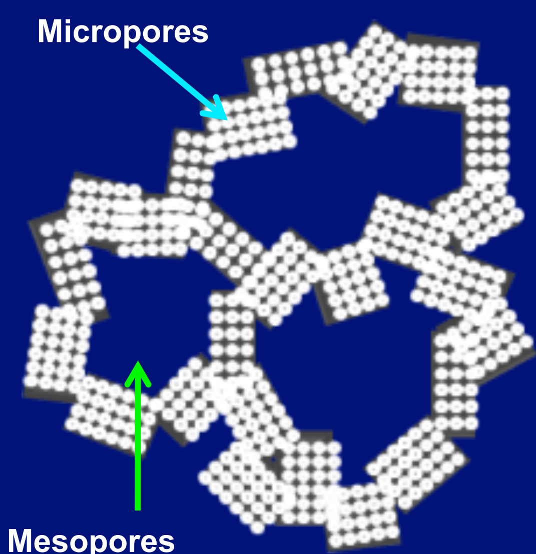


(J. Roggenbuck *et al.*, *J. Am. Chem. Soc.*, 2005, *127*, 1096)

Electric Double Layer Capacitor (Supercapacitor)



Hierarchically microporous-mesoporous carbon

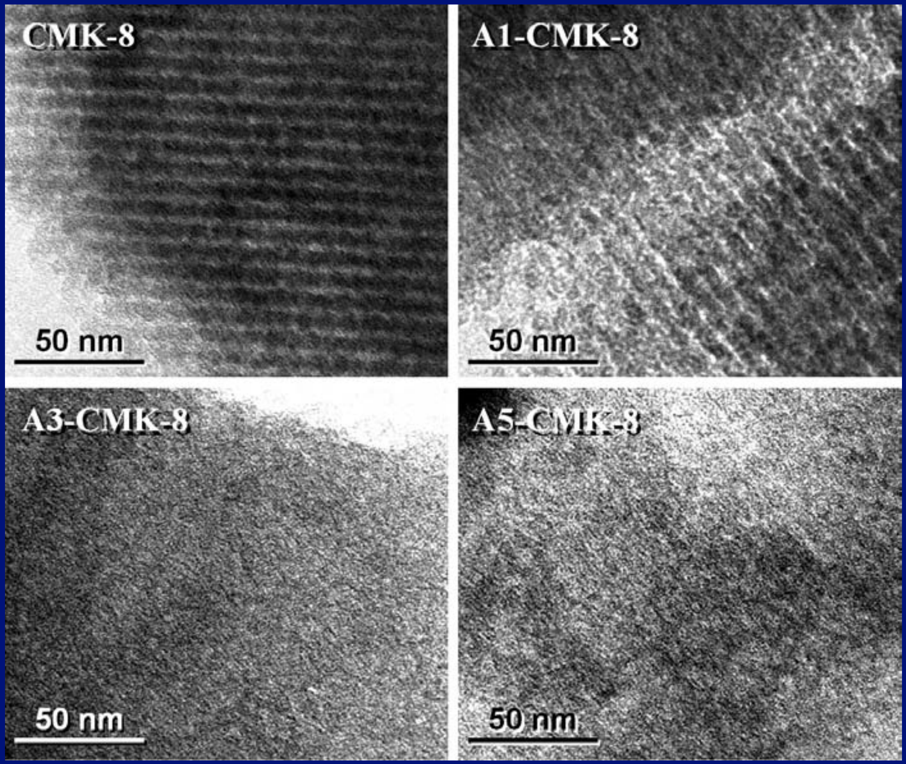


high capacitance even at high dis
charge current density

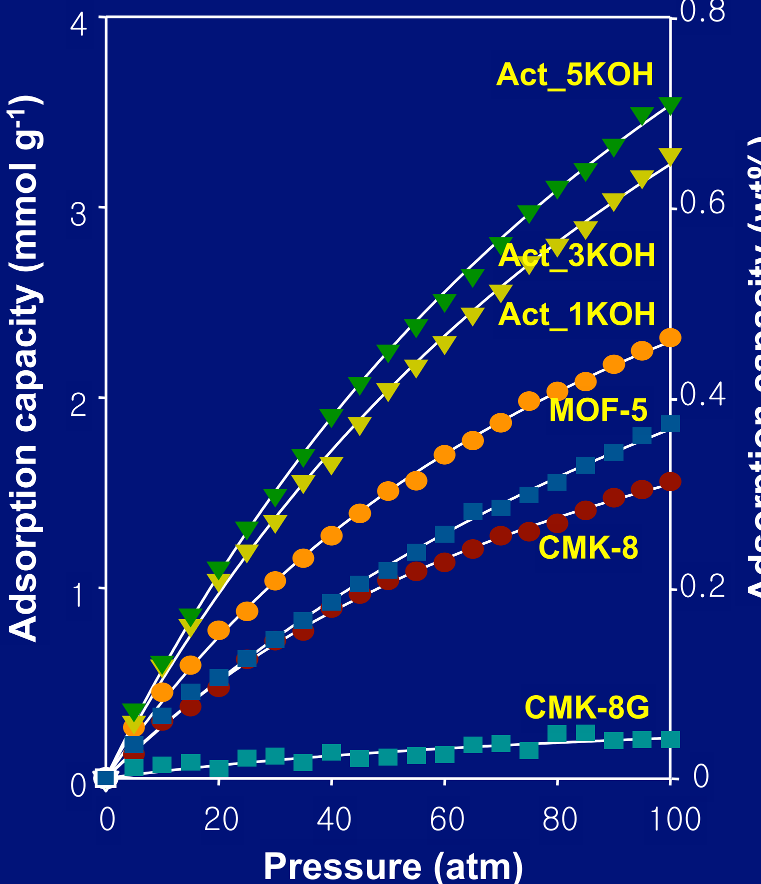
Hydrogen Uptake by Nanoporous Carbons - *"However, not yet suitable for hydrogen storage"*

KOH Activation

$4\ KOH + C \rightarrow 4\ K + CO_2 + 2\ H_2O$



Hydrogen adsorption at 298K

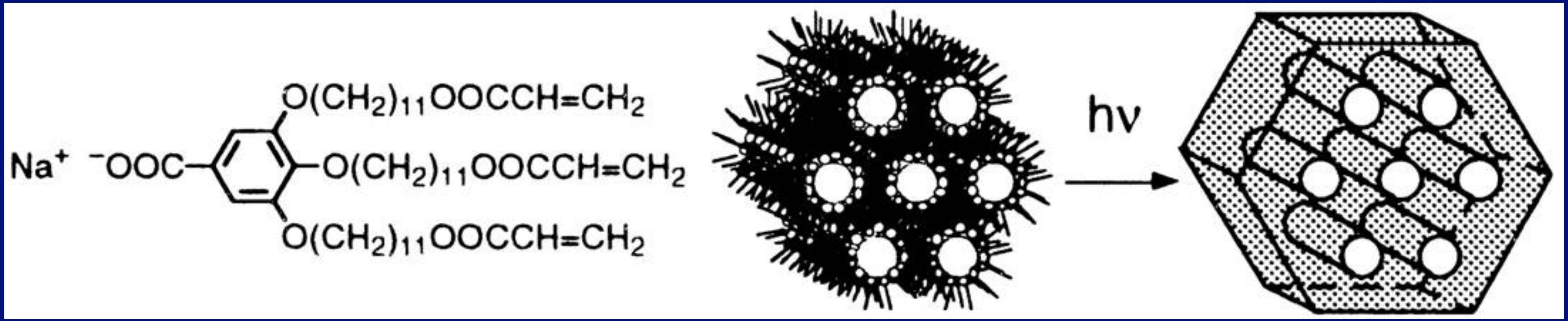


(M. Choi *et. al.*, *J. Mater. Chem.* 2007, *17*, 4204)

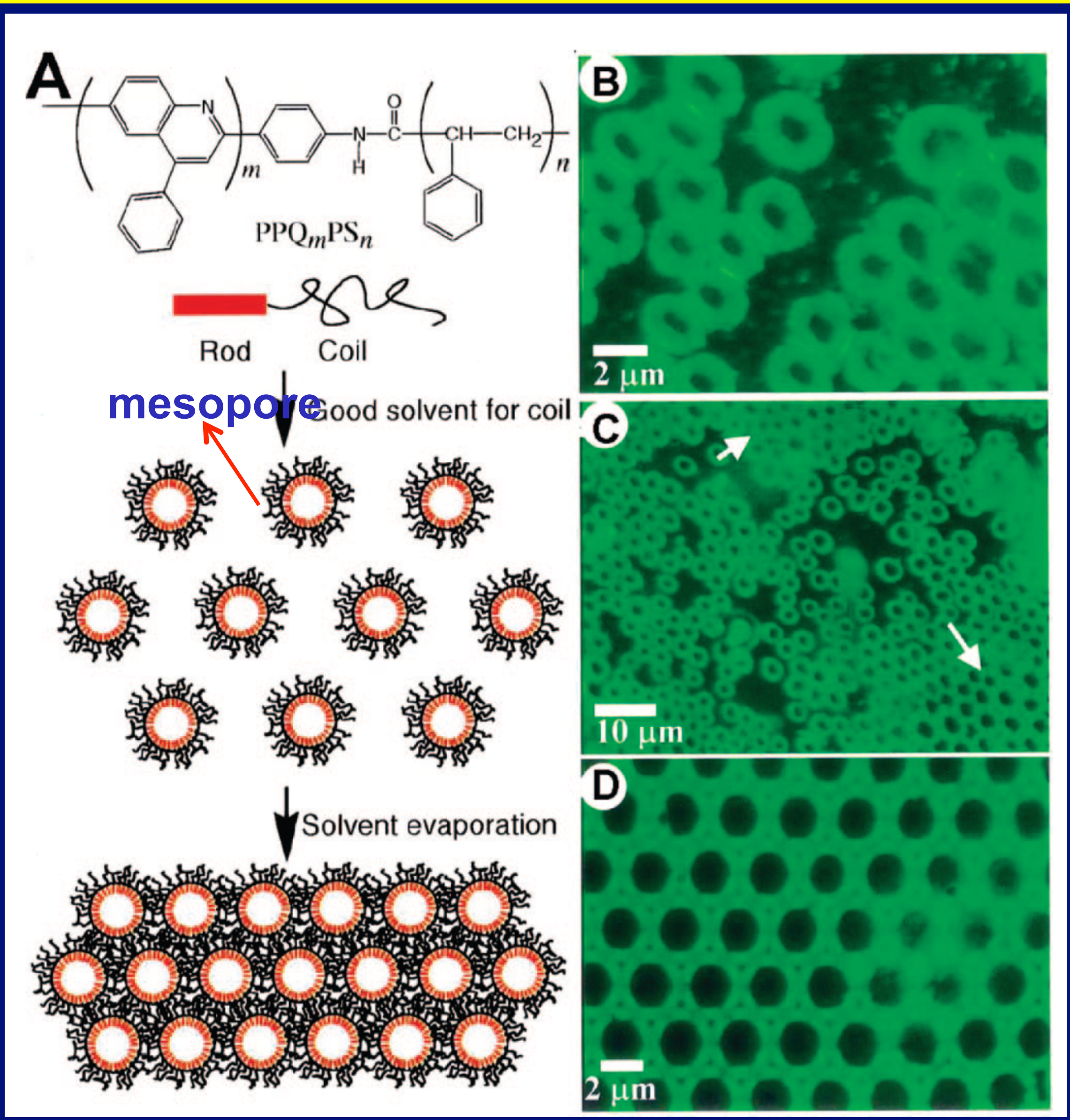
Mesoporous Polymers

Synthesis of Mesoporous Polymer:
Self-Assembly of Crosslinkable Surfactants

R. C. Smith et al.,
***J. Am. Chem. Soc.* 1997, *119*, 4092**



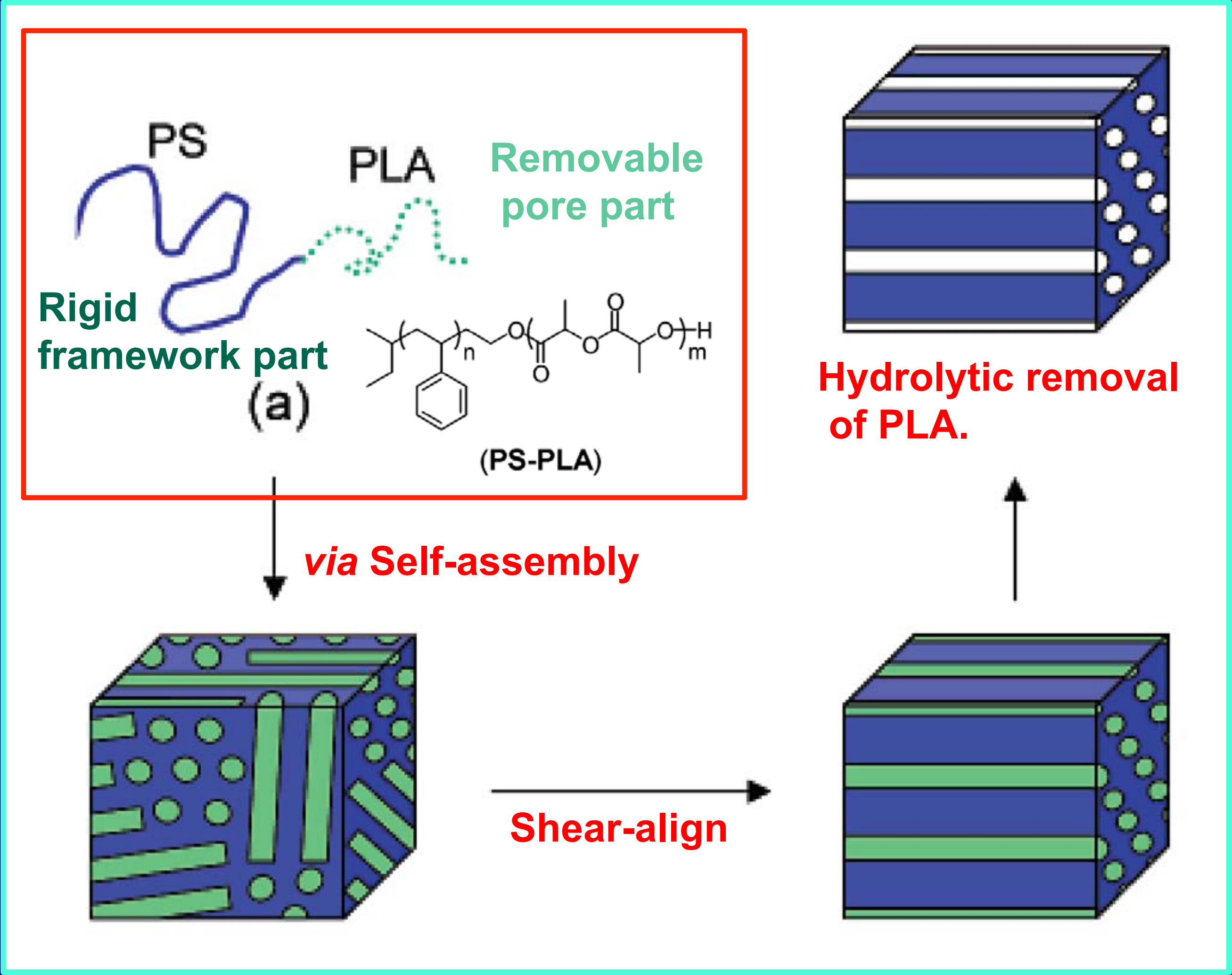
Self-Assembly of Rod-Coil Diblock Copolymers to form Hollow Sphere Micelles

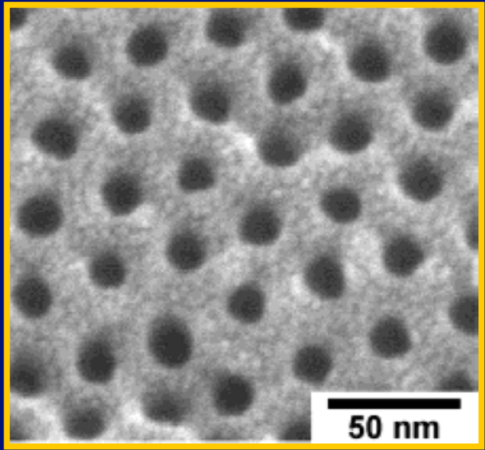


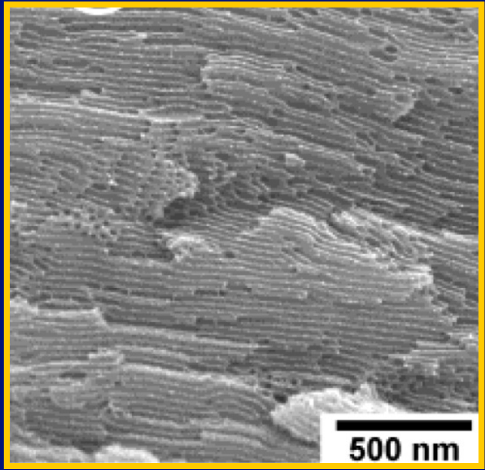
S.A. Jenekhe et al., *Science* 1999, *283*, 372

Self-Assembly of Block Copolymers followed by Decomposition of One Block

Using block copolymer which is composed of rigid block and removable block as mesopore generators and precursors, simultaneously♪



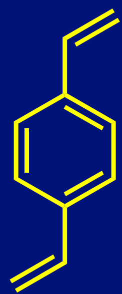




A.S. Zalusky et al., *J. Am. Chem. Soc.* 2002, *124*, 12761

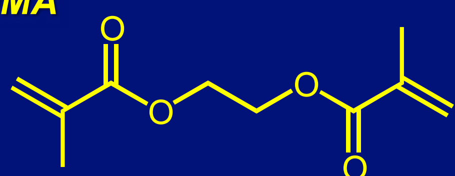
Use of Ordered Mesoporous Silica Template

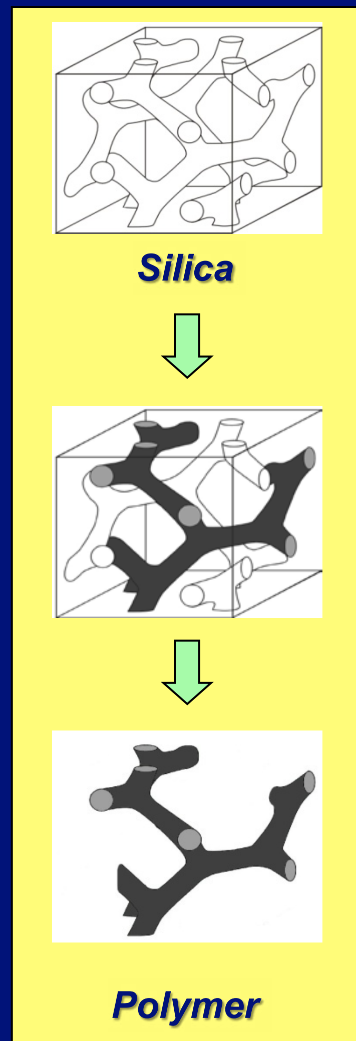
DVB

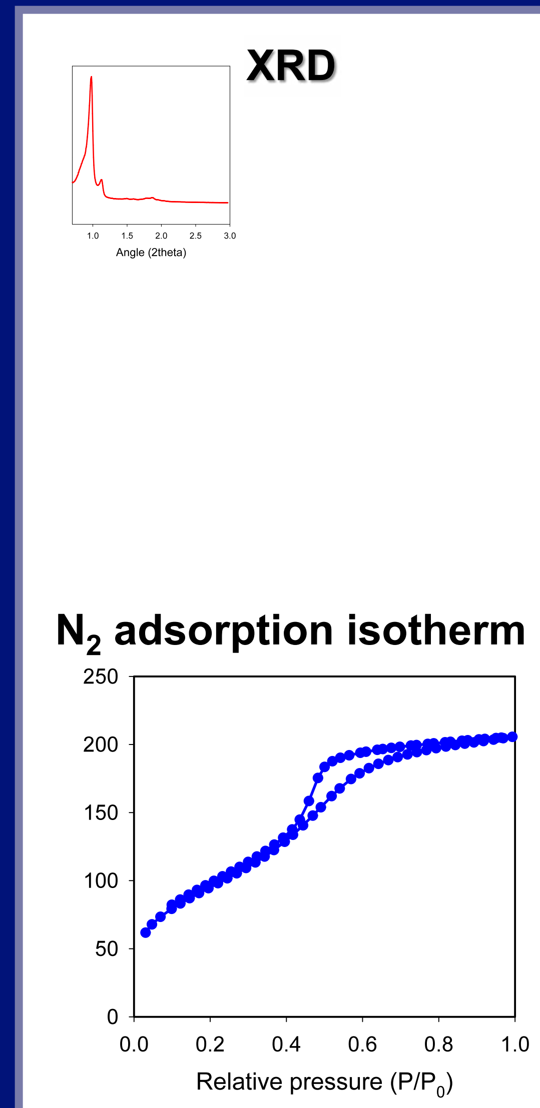


TMPTMA

EGDMA





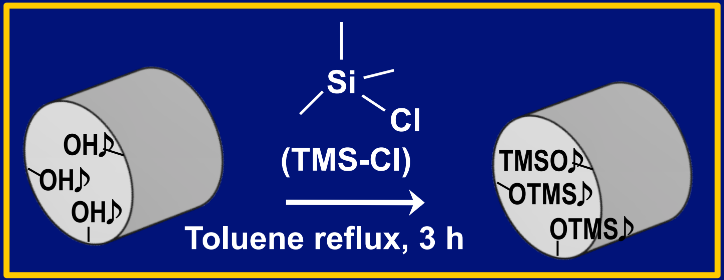


(D.-H. Choi et al., *J. Mater. Chem.* 2010, *20,* 5544)

Helpful Tips for Use of Ordered Mesoporous Silica Template

[J.Y. Kim et al., *J. Mater. Chem*. 2001, *11*, 2912] was difficult to reproduce.

(1) For hydrophobic monomers, silylation on the template pore walls



(2) Uniform Impregnation of DVB and AIBN using CH_2Cl_2 solution

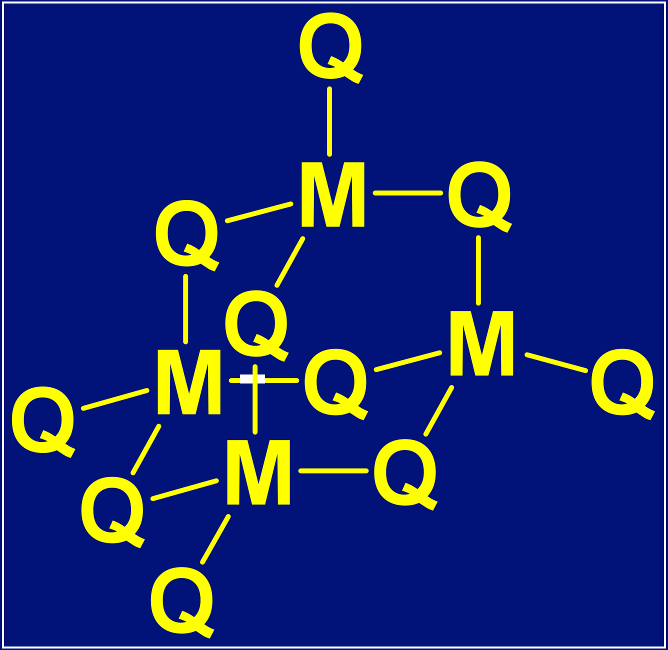
(3) Freeze-vacuum-thaw treatment for more uniform impregnation

(4) Radical polymerization with heating

(5) Template removal by HF solution

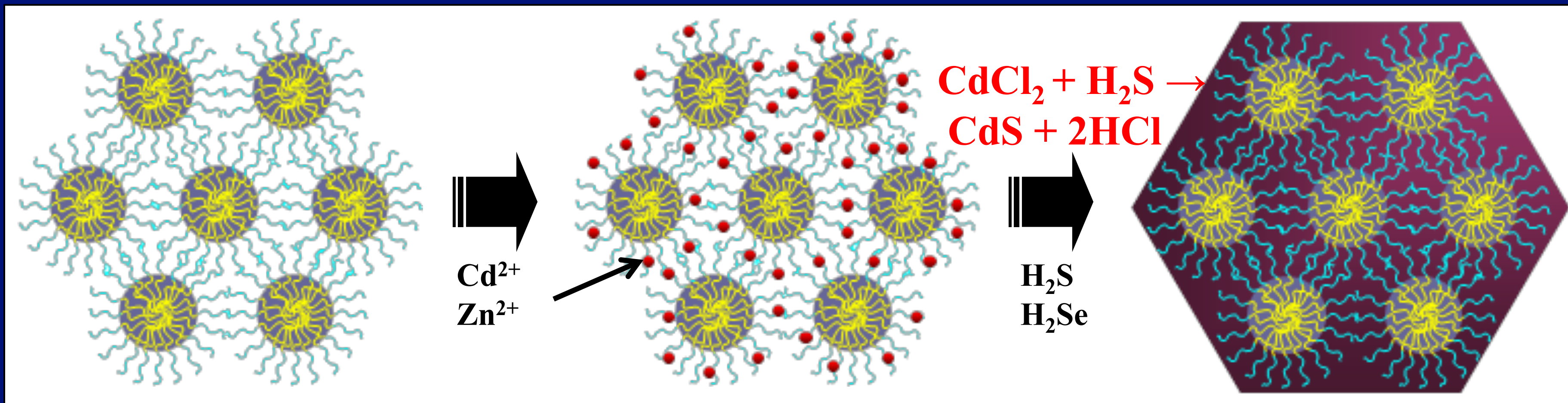
See D.-H. Choi et al., *J. Mater. Chem.* 2010, *20,* 5544 for details

Chalcogenides



M = Zn, Ge, Sn, In, etc
.
Q = S, Se, Te, etc.♪

Liquid Crystal Templating Route to Mesostructured Chalcogenide



Self-assembled surfactant micelles

Organic-inorganic nanostructured composite

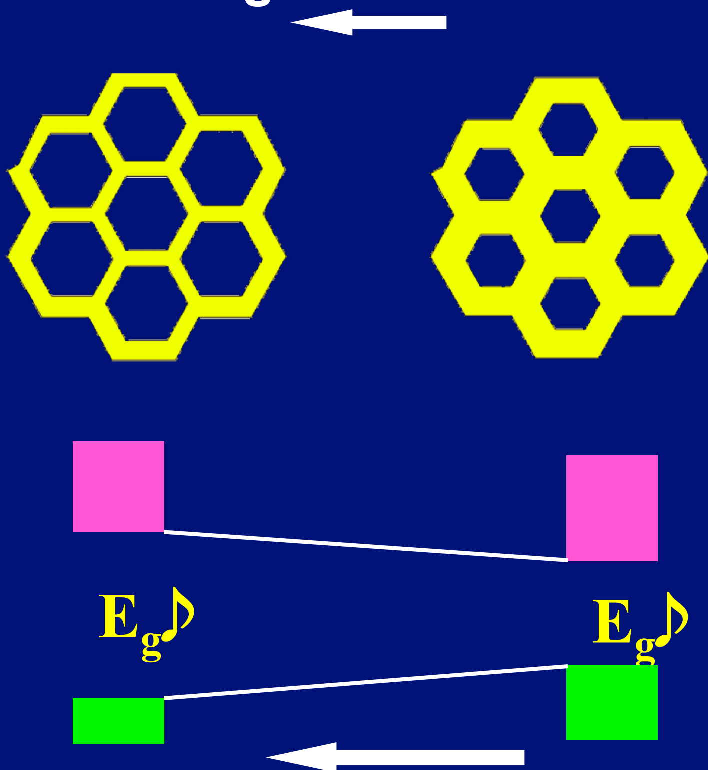
CdS, CdSe, ZnS nanoparticles or nanopores

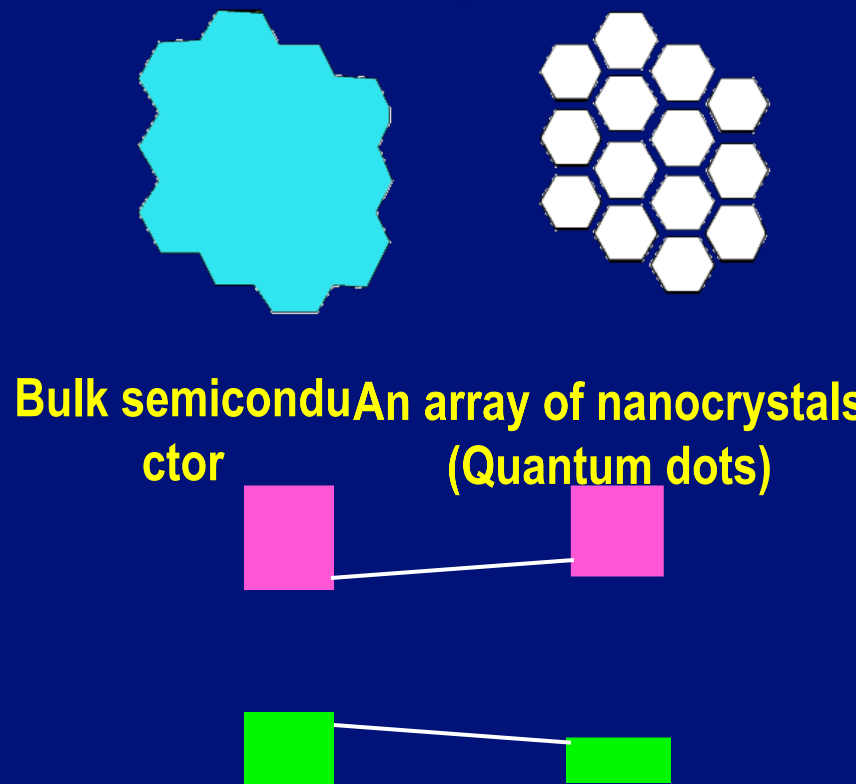
M. Bawendi
CdSe Quantum Dot (1993)

Design of surfactants is very important for control of mesostructure and optoelectronic properties

Band Gap Evolution of Chalcogenides

Decreasing wall thickness & pore size





Increasing the bandgap energy (E_g) & blue shift

M. G. Kanatzidis group, *Adv. Mater.* 2007, 19, 1165

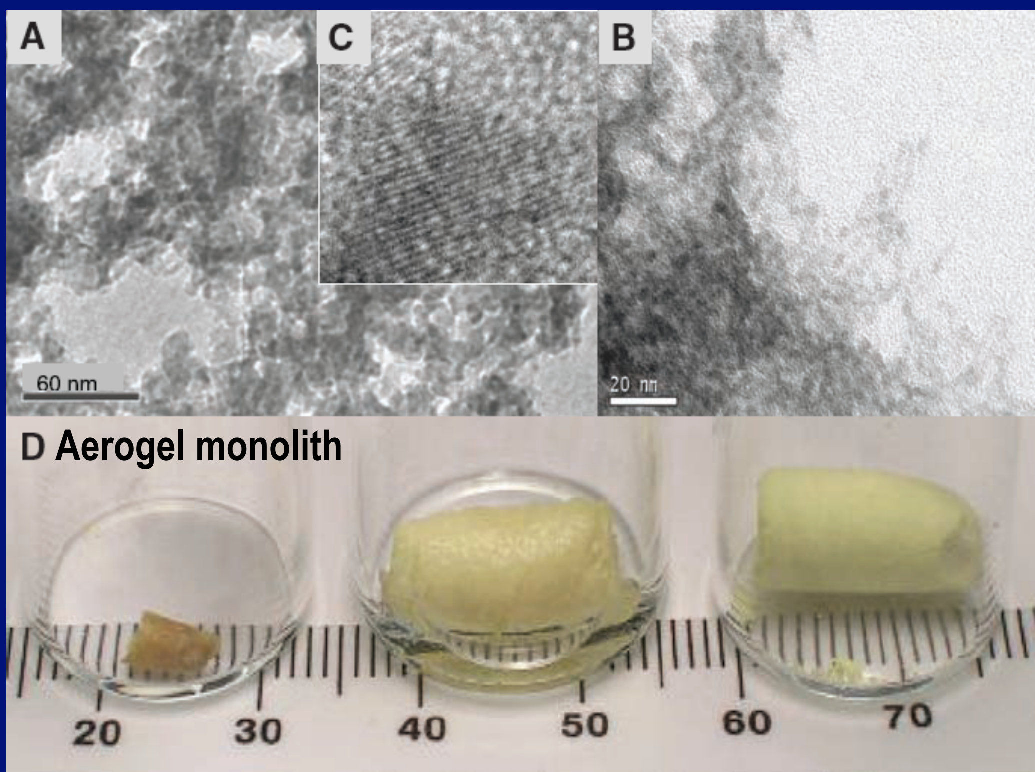
(D. Weiss et al., *Phys. Rev. Lett.* 1993, *70*, 4118)

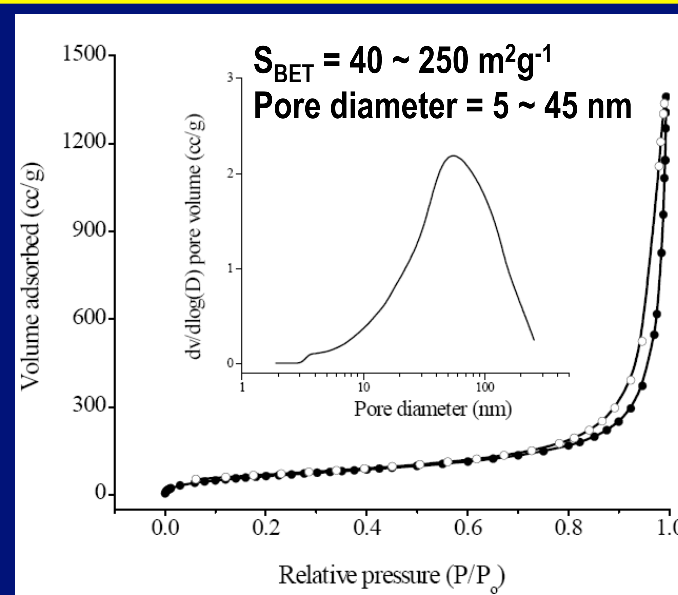
Chalcogenide Nanoparticles or Nano porous Chalcogenides

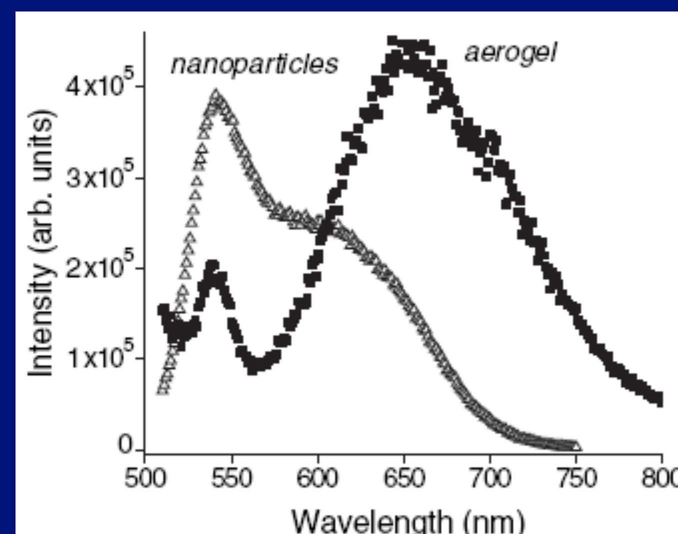
- Semiconducting superlattices
- Tunable electronic and photonic properties
  (color display)
- Open porous structures →
  adsorption & ion-exchange (sensor)

Mesopore generation in chalcogenide: Aerogel

1. Nanoparticle formation/thiolate capping
2. Gelation through controlled surface-group (thiolate) loss
3. Supercritical CO_2 drying
4. Assembly of chalcogenide nanoparticles
5. Chalcogenide aerogel

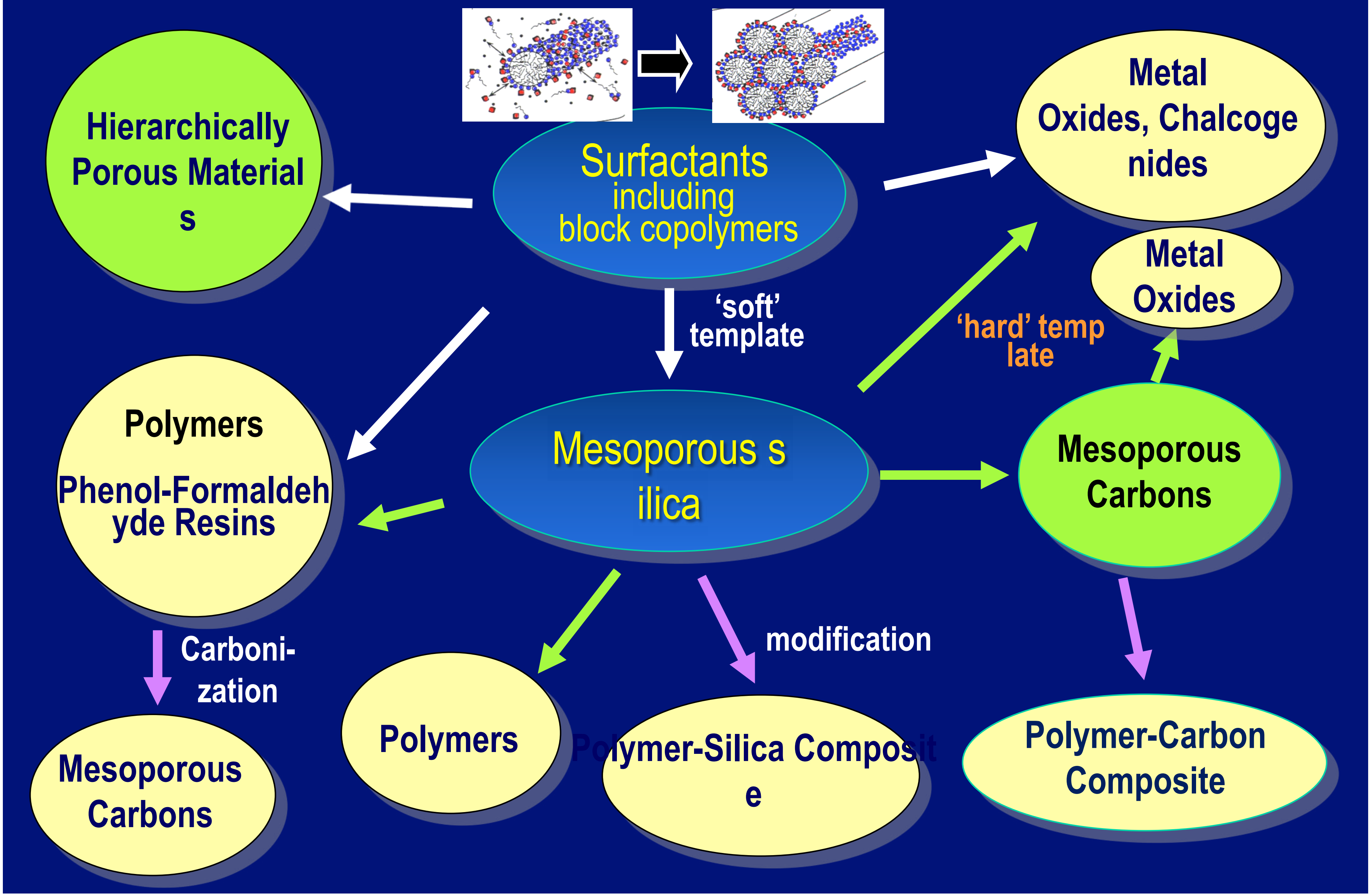






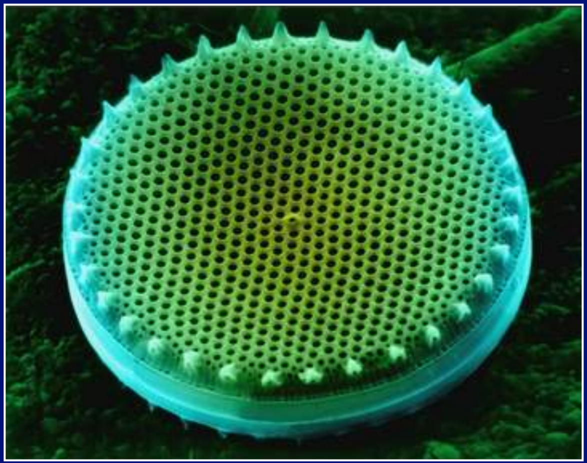
(J. L. Mohanan et al, *Science* 2005, *307*, 397)

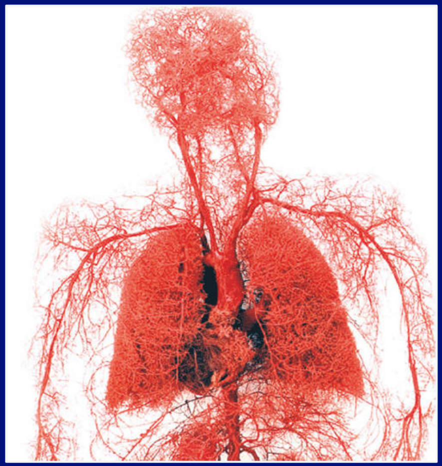
Various Materials Available via Surfactant-Assembling Route and Hard-Templating Route

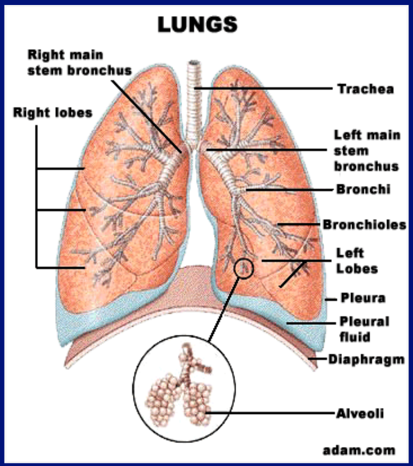


Hierarchical Pore Systems

'Maximized function in a limited space' due to facile transport







General Strategy: Use Two or More Kinds of Pore-Generating Agent (Porogen)

- Pore generation is a thermodynamically unfavorable, energy-consuming & entropy-lowering process.

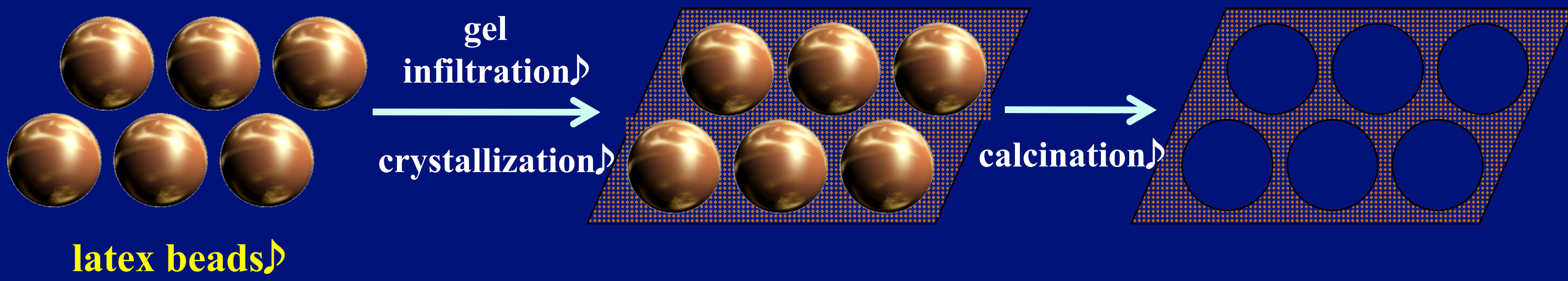
- One or several kinds of pore-generating agent (porogen) may be used to generate pores at different levels of pore size.

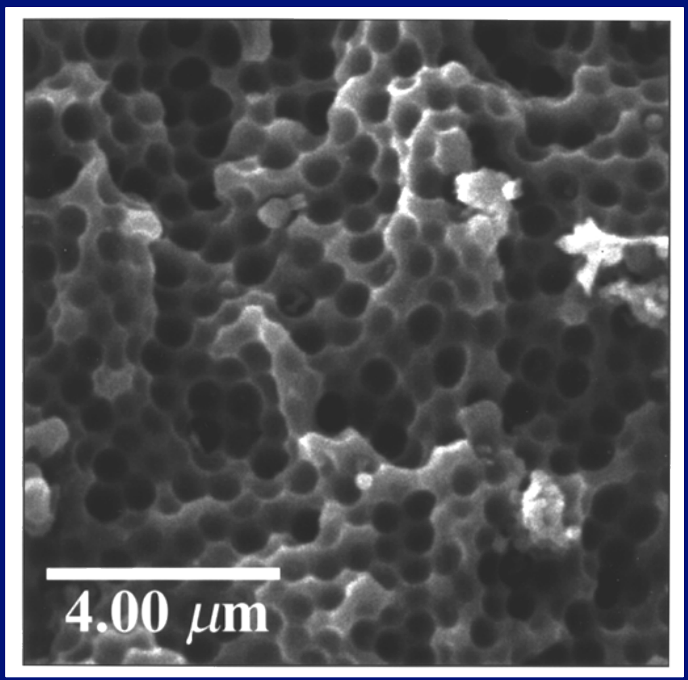
- Porogens are very often miscible.
Use immisible porogens (hard-soft, hard-hard, soft-soft, etc.)

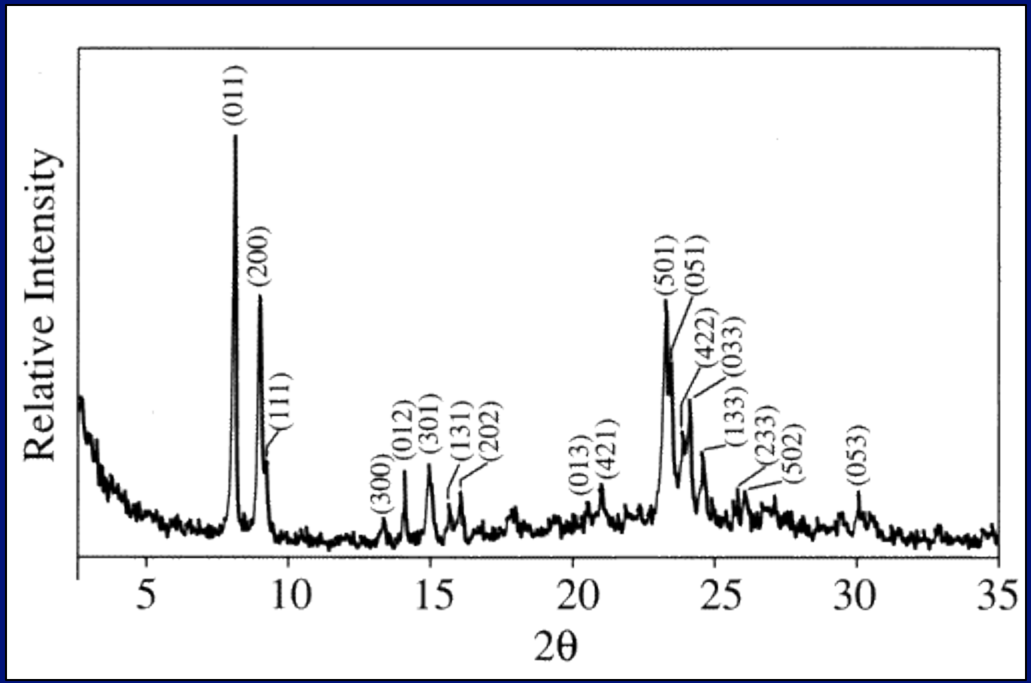
- Separation of product phases are very common even if immisible porogens are used.

- Macro-Micro is easier > Macro-Meso > … > Micro-Micro Hierarchy

Example: Polymer Nanobeads for Macropores & Tetrapropylammonium$^+$ for Zeolite Micropores



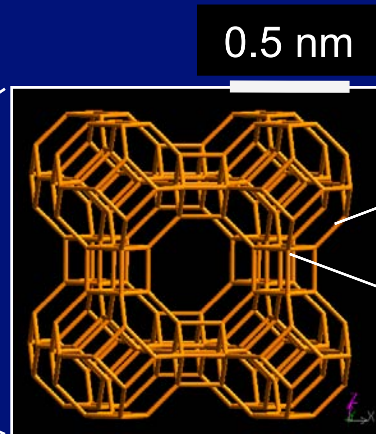


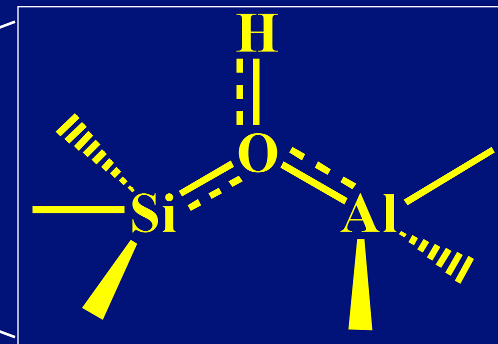


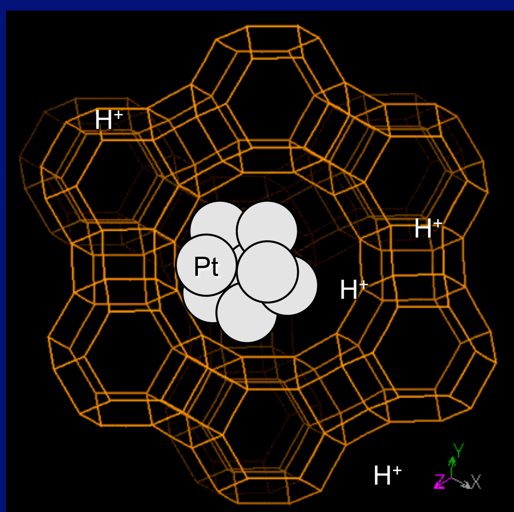
A. Stein, J. Am. Chem. Soc., 1999, 121 4308

Zeolite

Natural or Synthetic







Crystalline microporous aluminosilicate minerals

- Uniform micropores (0.3~1.5nm) with molecular dimension
- Molecular sieving effect → size/shape-selectivity
- High hydrothermal stability
- Cation exchange capacity
- Strong acidity of the H^+ form → acid catalytic activity

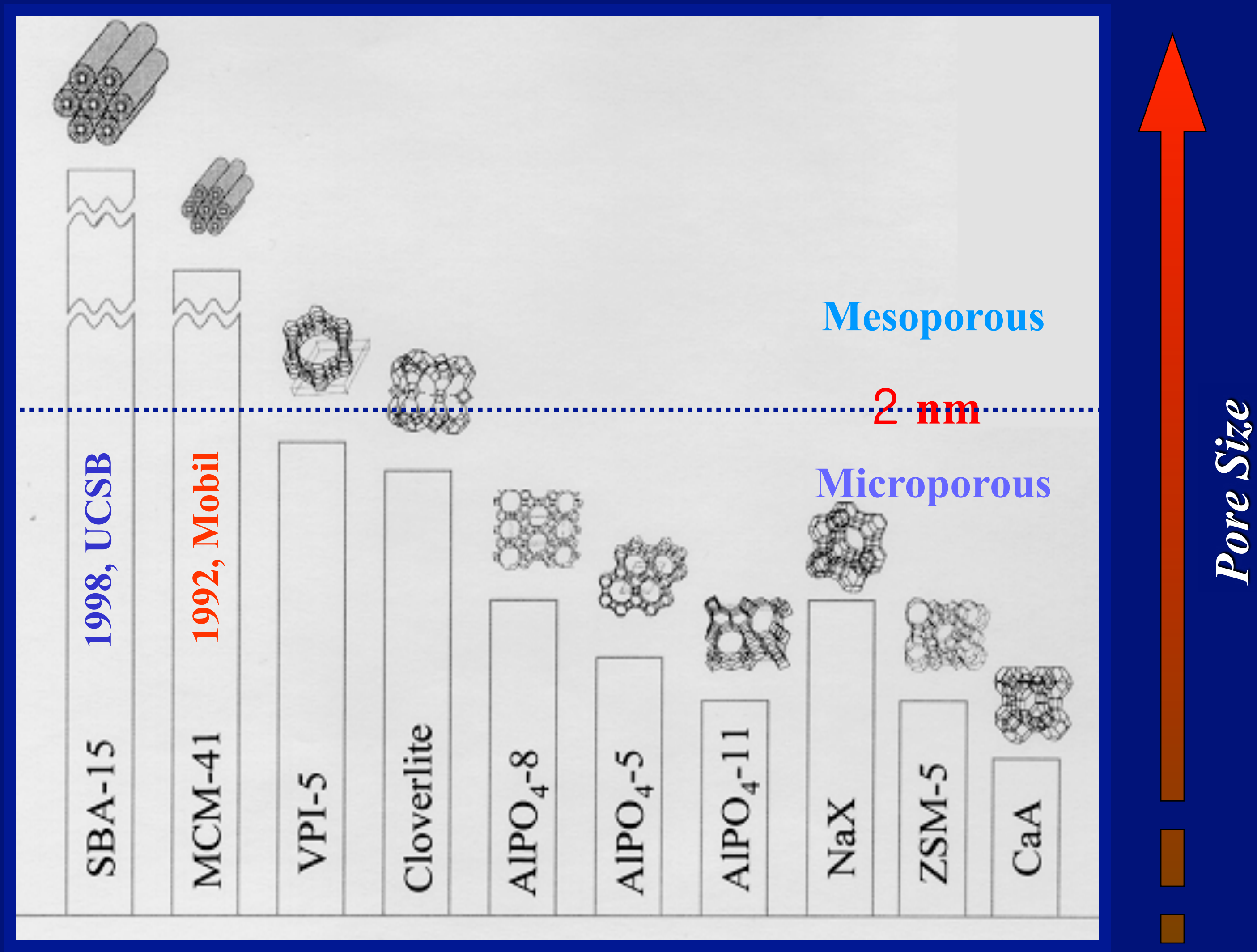
Applications:

shape-selective adsorbent, acid catalyst, catalyst support

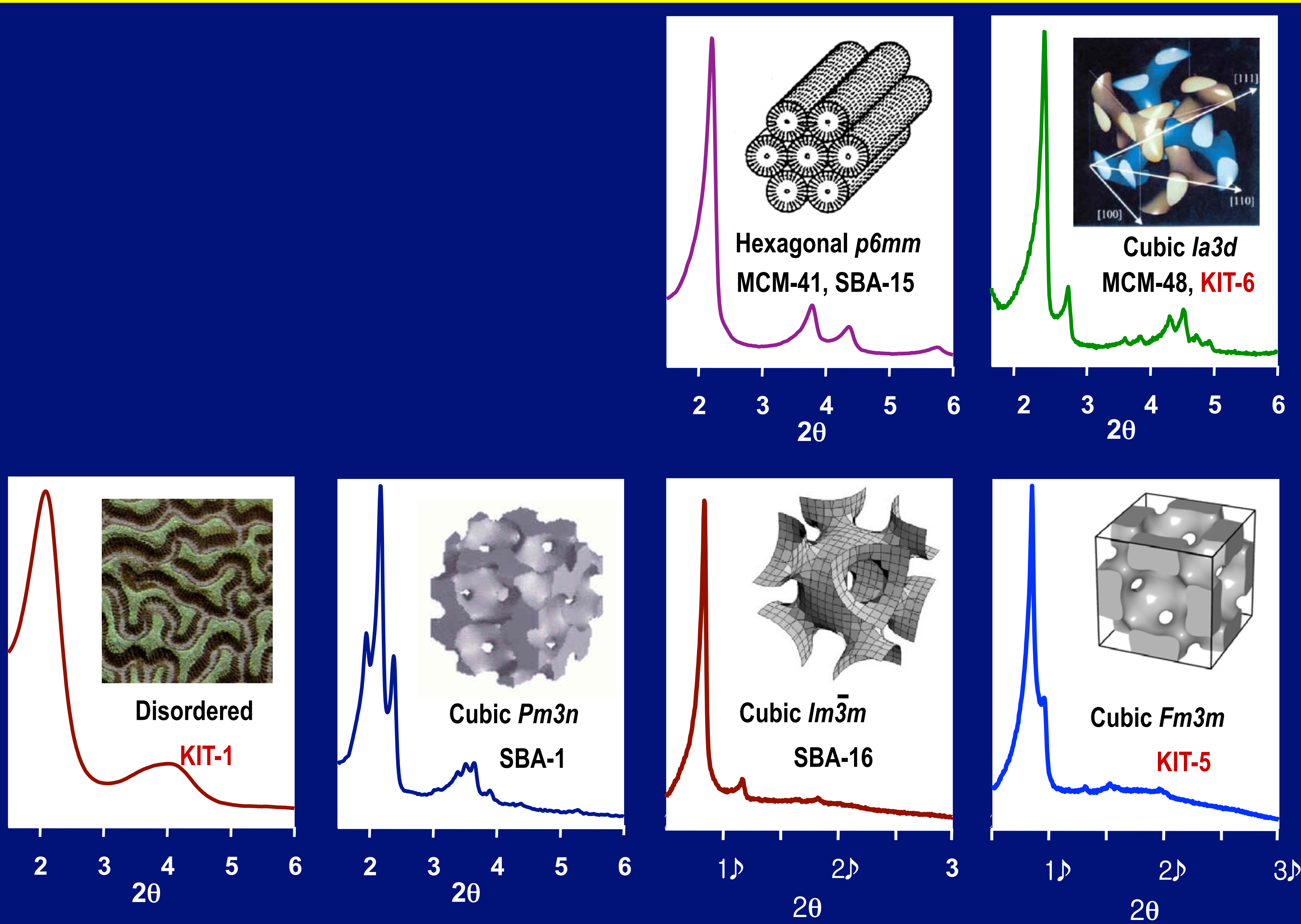
- FCC catalyst for gasoline production,
- other petrochemical reactions,
- organic syntheses

However, zeolite pores are too narrow for bulky molecules.

Ordered Nanoporous Materials



Ordered Mesoporous Silica with Various Structures



The widely open mesopores of the MCM-41-like mesoporous silicate attracted much attention as adsorption and catalytic applications where zeolites suffered from diffusion limitation.

Aluminum could be incorporated into the siliceous framework, directly during synthesis, or through a post-synthesis route.

The aluminosilicate frameworks were not sufficient for many acid catalytic applications, due to non-crystalline nature.

In recent years, there have been many attempts to synthesize mesoporous materials that are built with crystalline zeolitic pore walls.

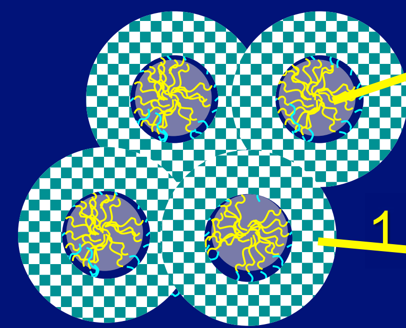
Addition of CTAB-Type Surfactants into Zeolite Synthesis Composition

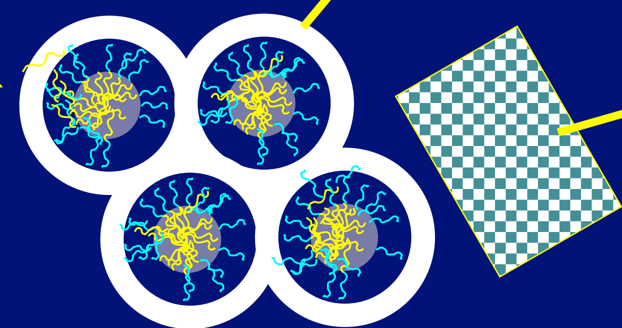
Zeolite Synthesis Composition:

H_2O, SiO_2 & Al_2O_3 sources
micropore-directing agent
(e.g., amines, Na^+)

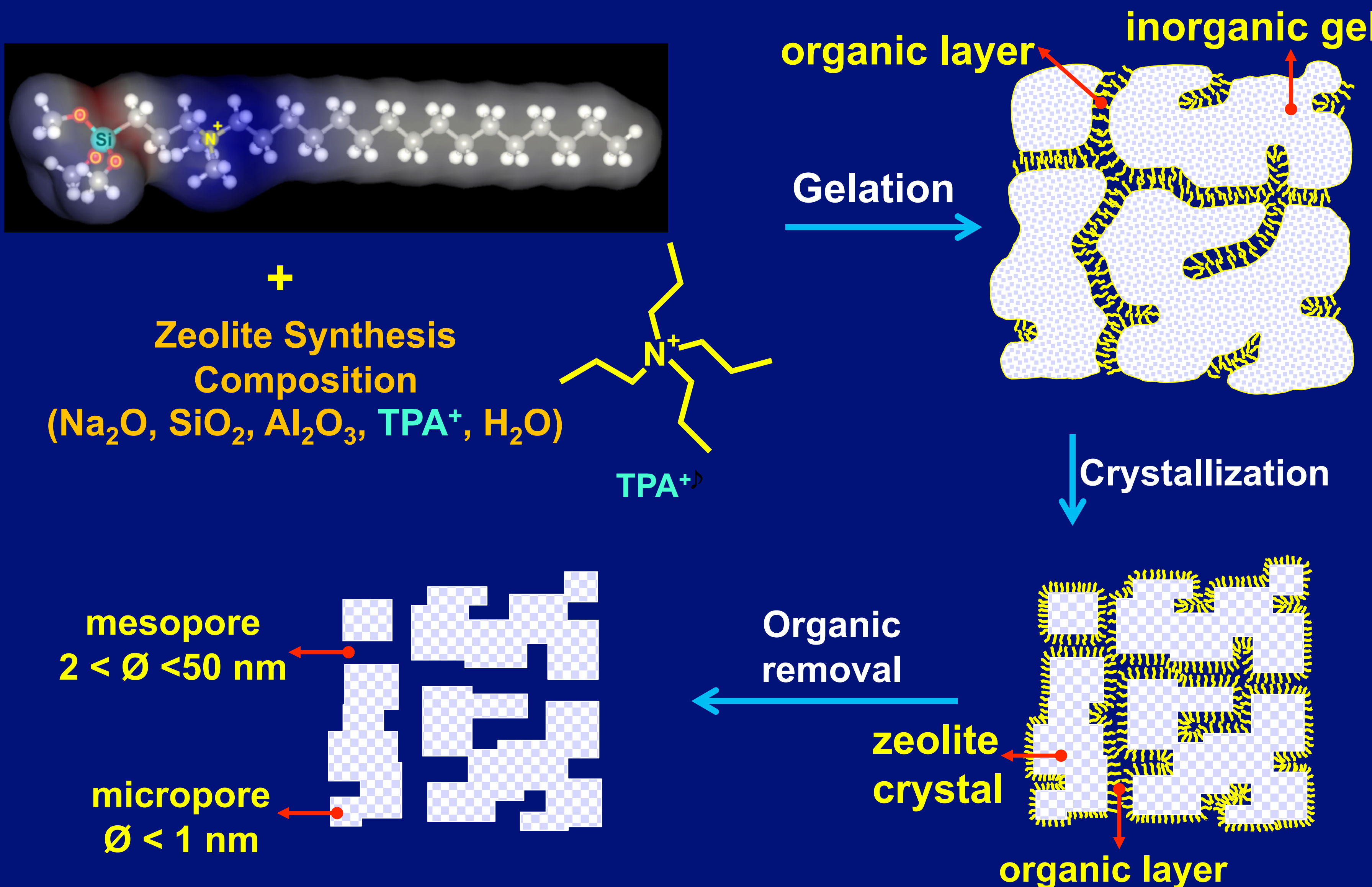
+

CTAB-Type Surfactant as a mesopore-generating agent



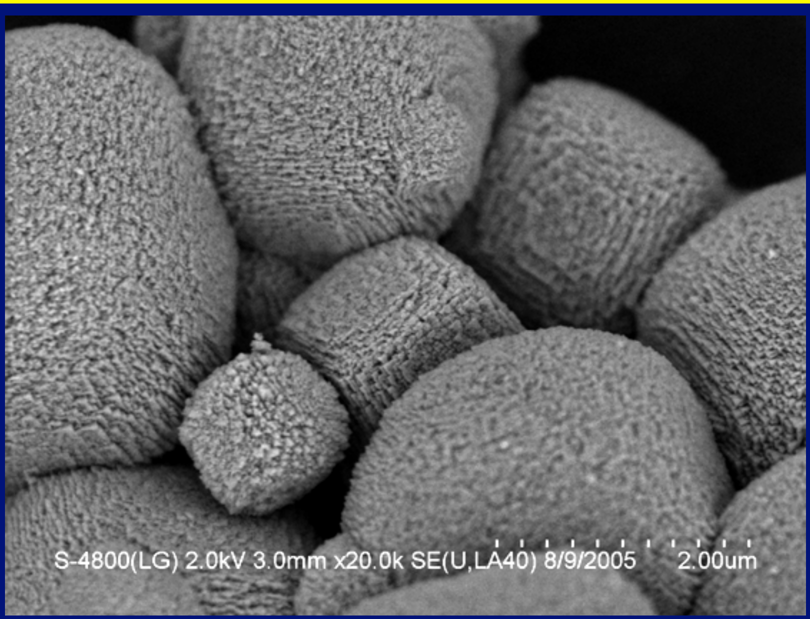


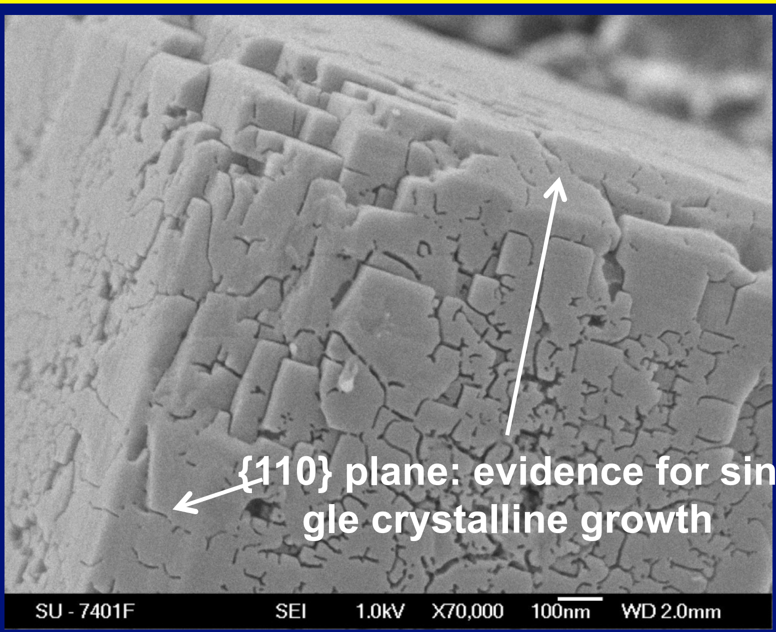
Addition of Organosilane Surfactants into Zeolite Synthesis Gel

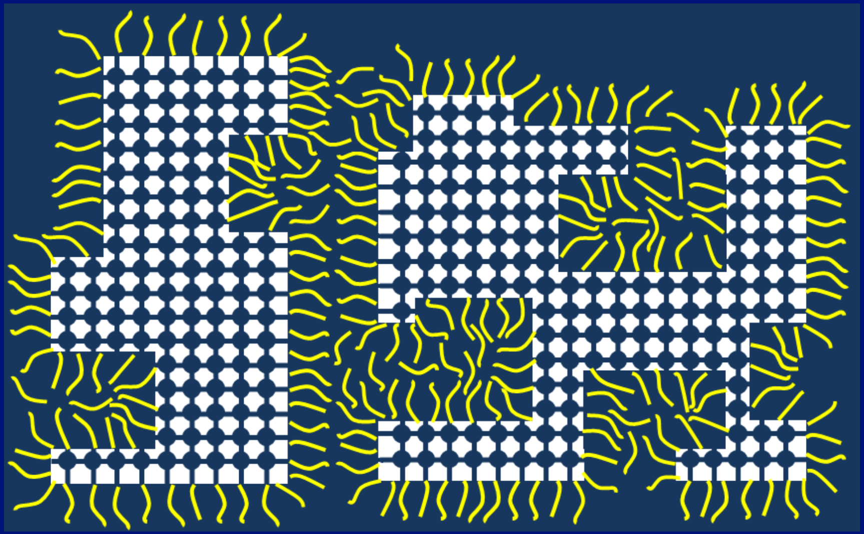


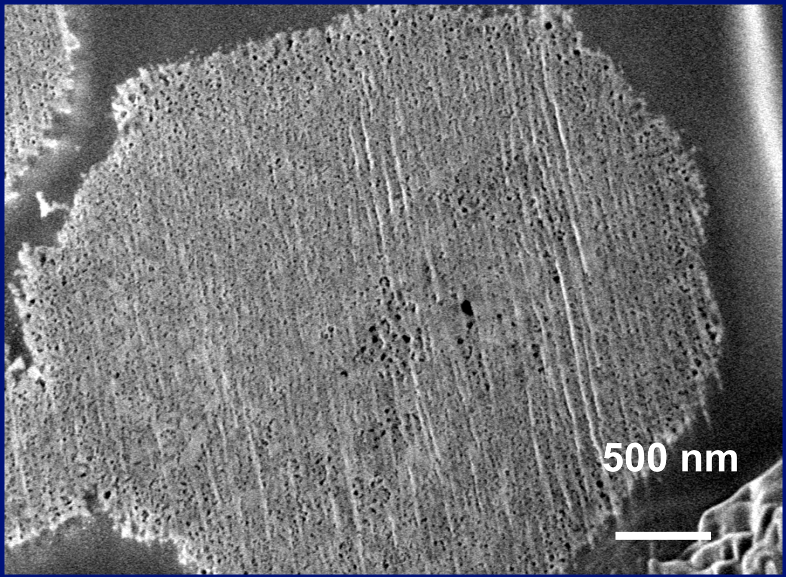
(M. Choi et al., *Nature Mater*. 2006, 5, 718)

HRSEM Images of Hierarchical NaA Zeolite



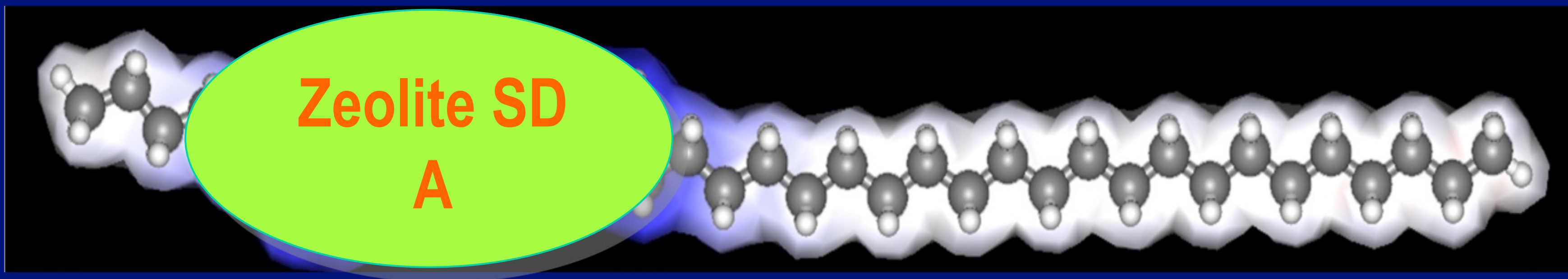


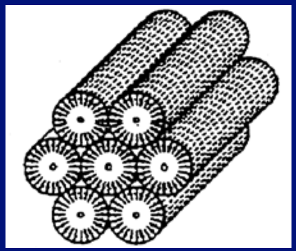


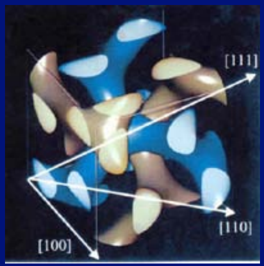


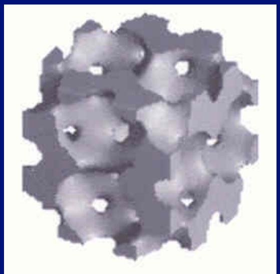
(K. Cho et al., Solid State Science, 2010)

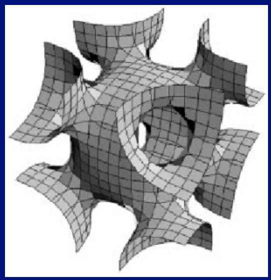
“Can we synthesize mesoporous materials using a surfactant that is functionalized with a zeolite-structure-directing agent (SDA)?”

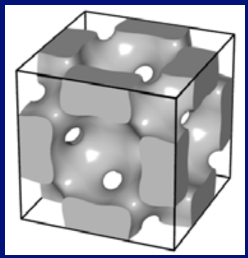






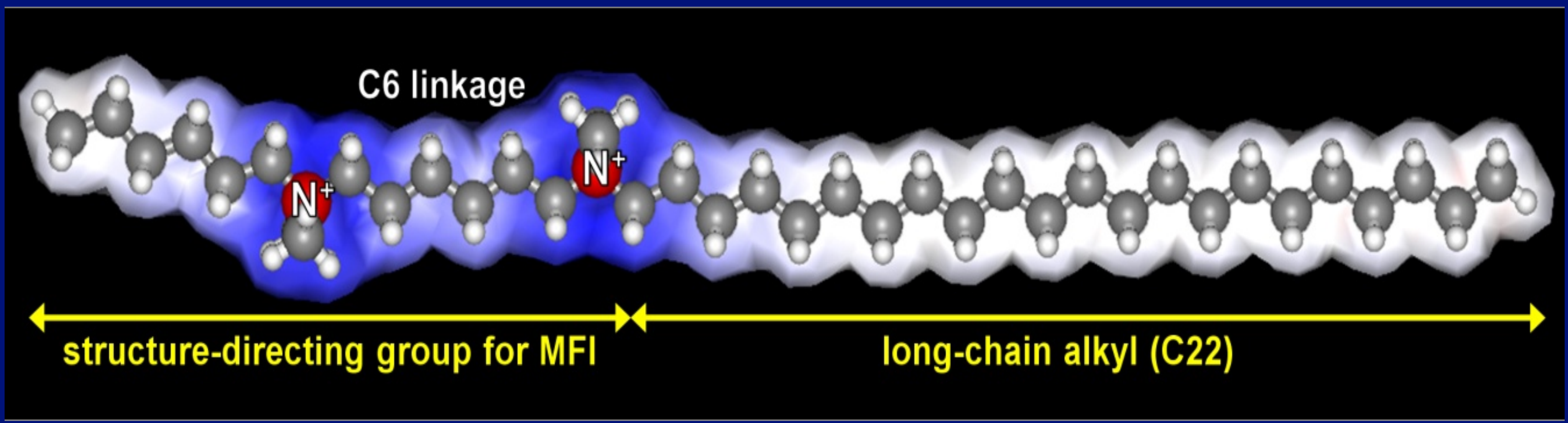






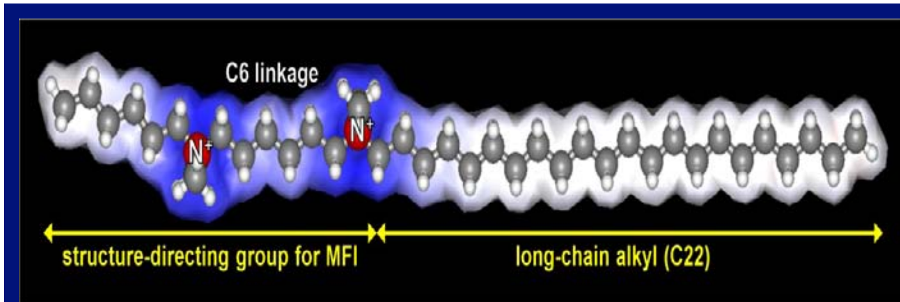
“Are these structures possible to synthesis with crystalline zeolite frameworks?”

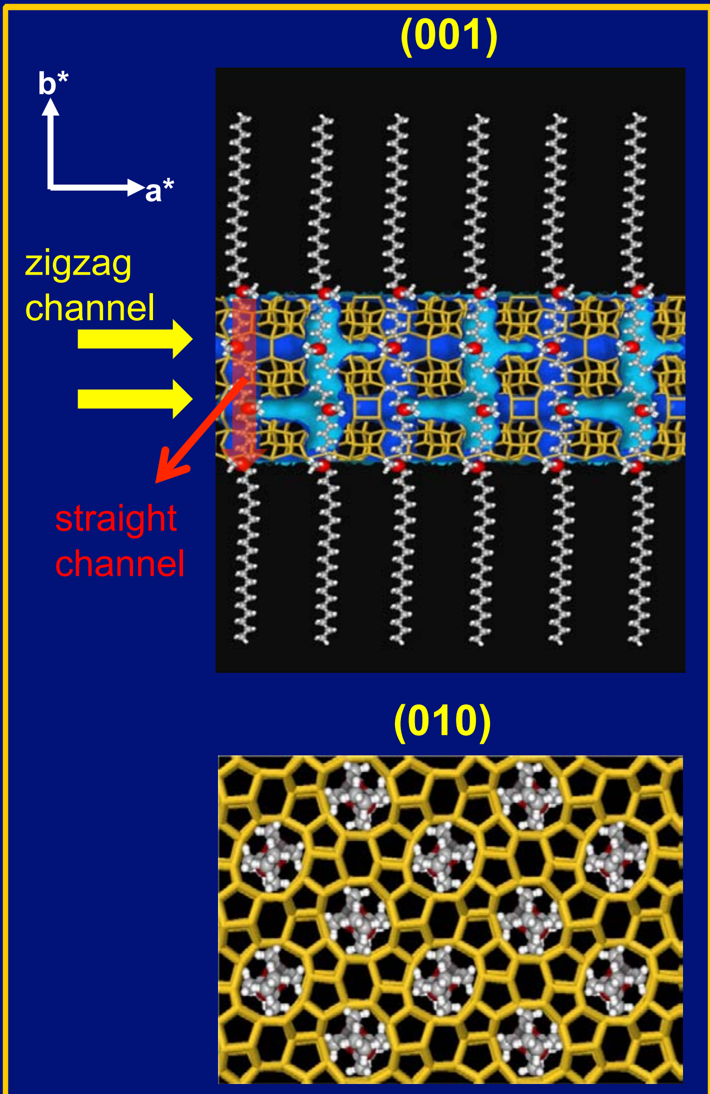
First Example: Hydrothermal Synthesis of Zeolite using

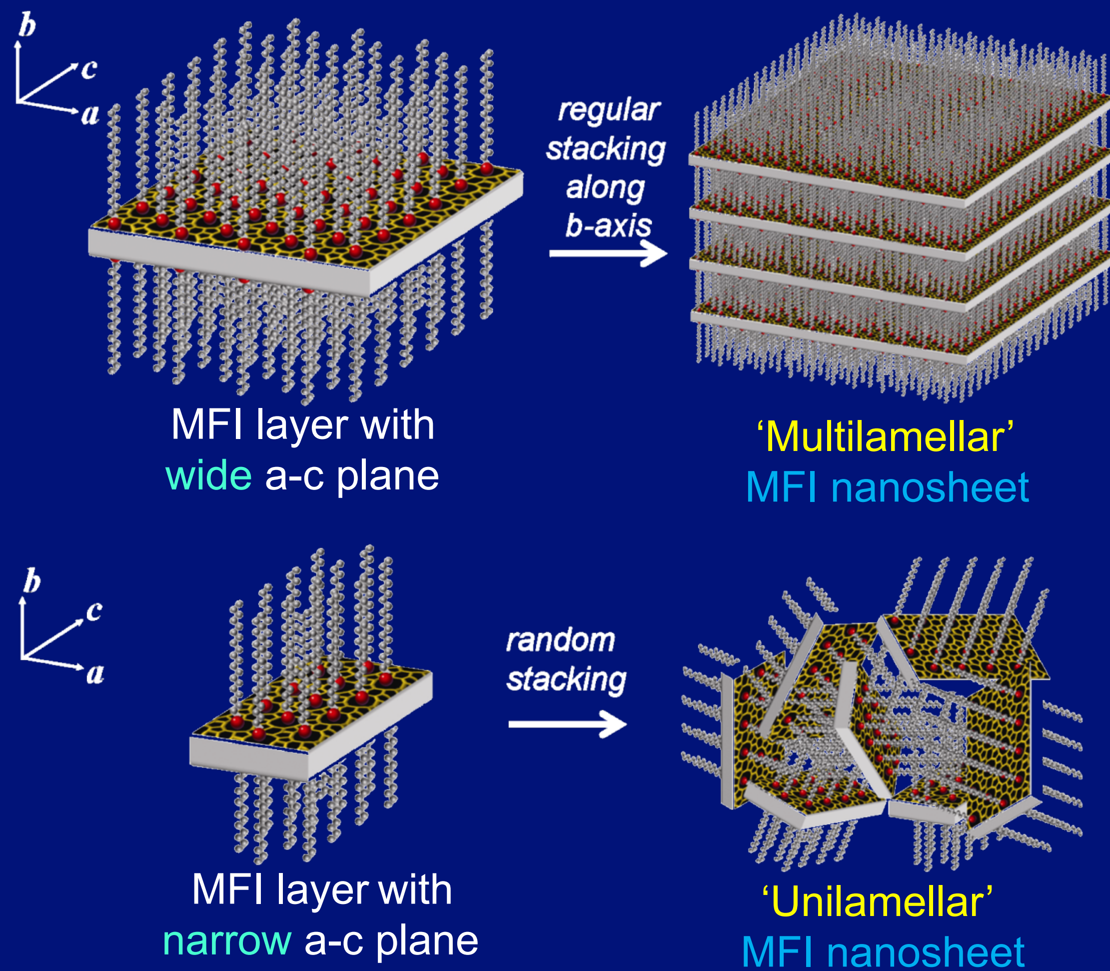


Result: MFI Zeolite Nanosheets of a Single-Unit-Cell Thickness

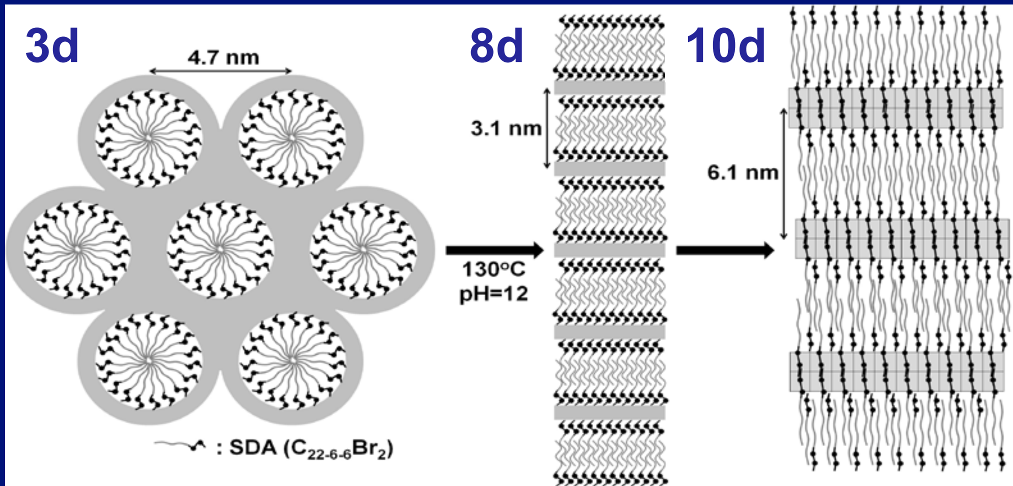
(M. Choi et al., *Nature* **2009**, 461, 246)

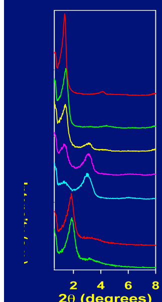




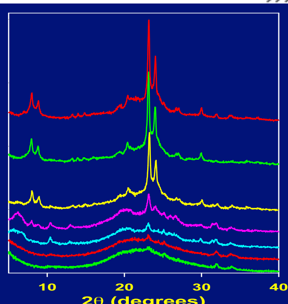


Consecutive Transformations for the Formation of Multilamellar MFI Zeolite

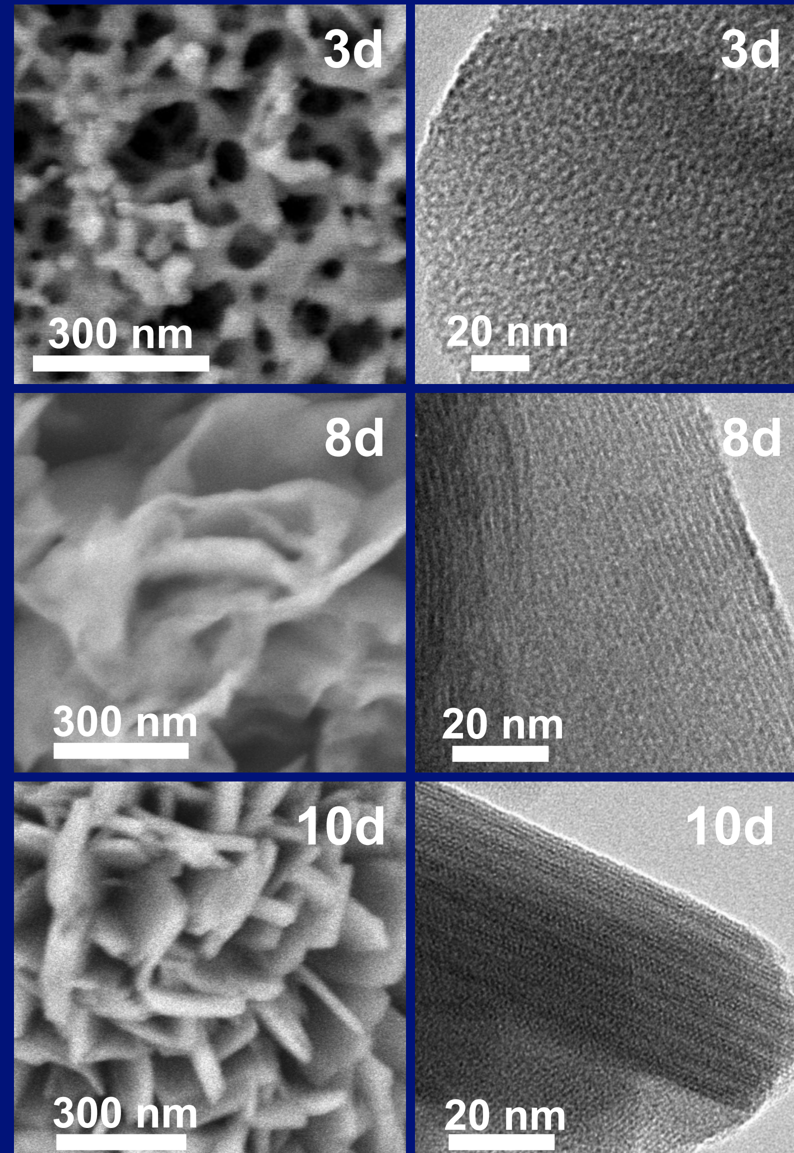




20 d
10 d
9 d
8.5 d
8 d
3 d
10 min

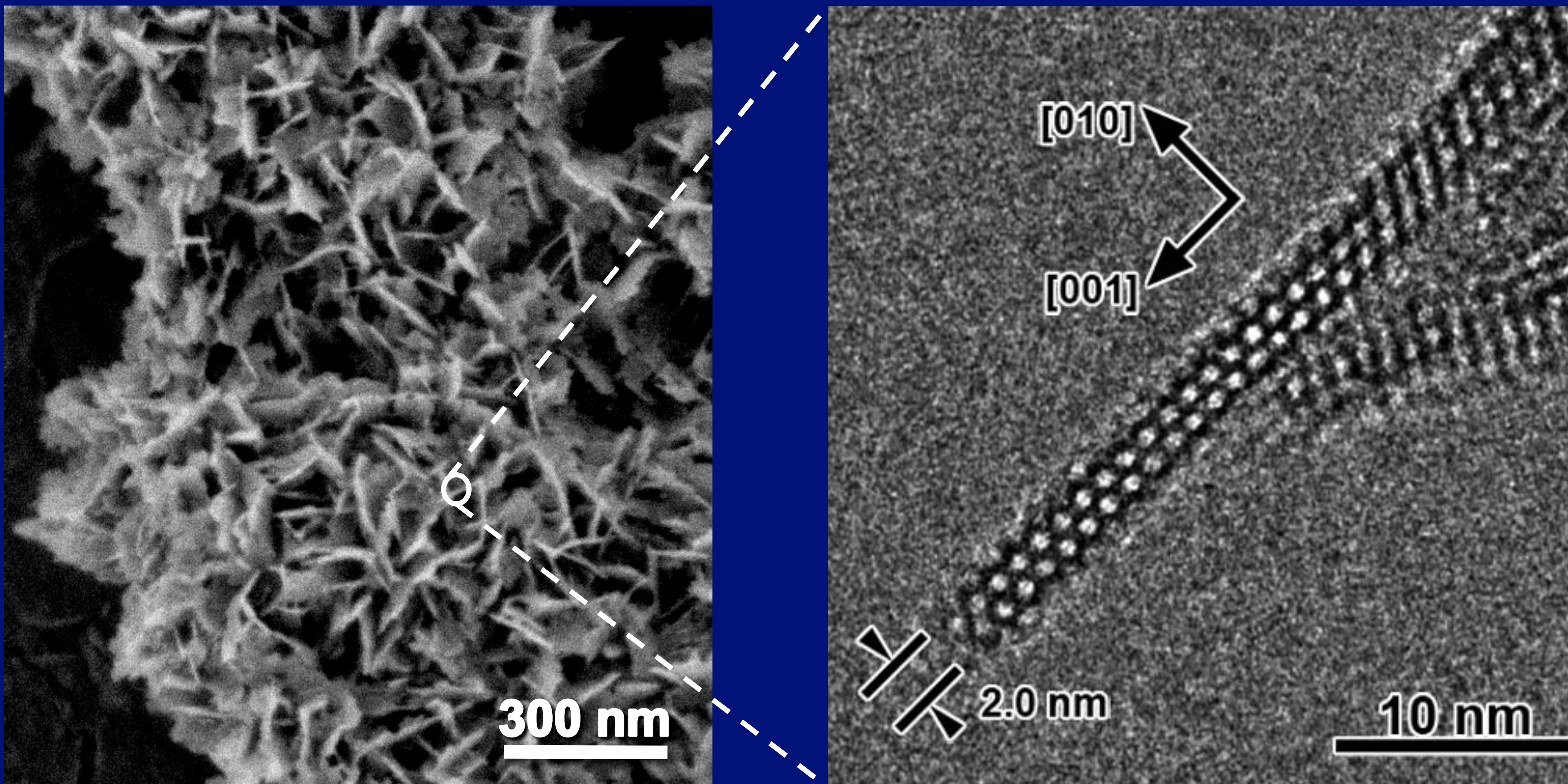


20 d
10 d
9 d
8.5 d
8 d
3 d
10 min



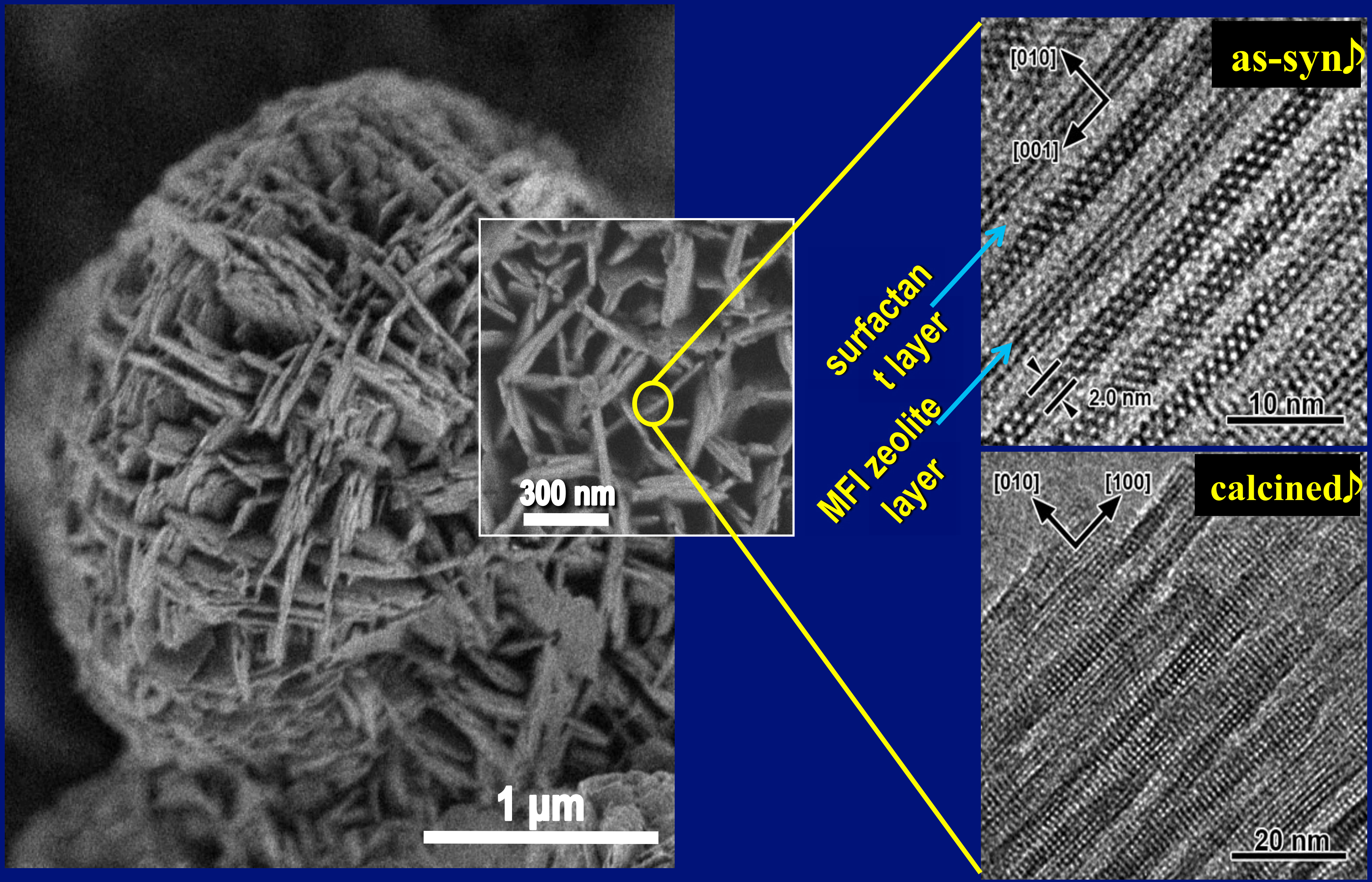
Kyungsu Na et. al. *J. Am. Chem. Soc.*, Ma
rch 31 in 2010

Zeolite MFI Unilamellar Nanosheets



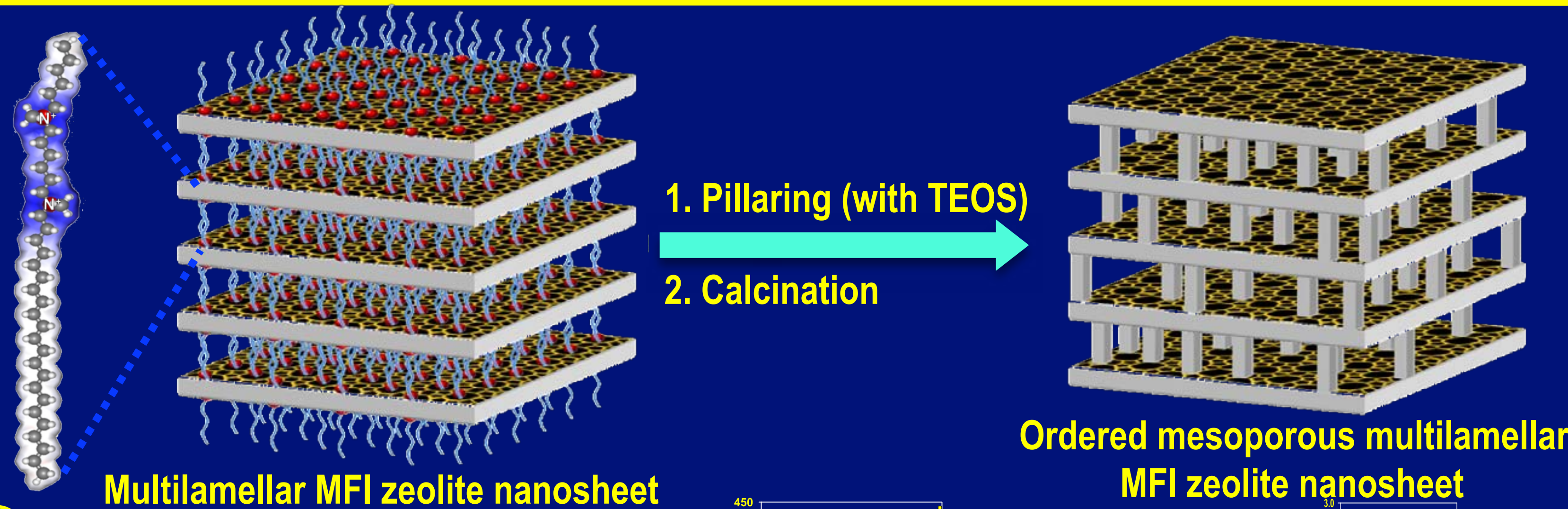
BET surface area ≈ 700 m^2/g
Total pore volume ≈ 1.0 cc/g
(conventional zeolite: 400 m^2/g & 0.3 cc/g)♪

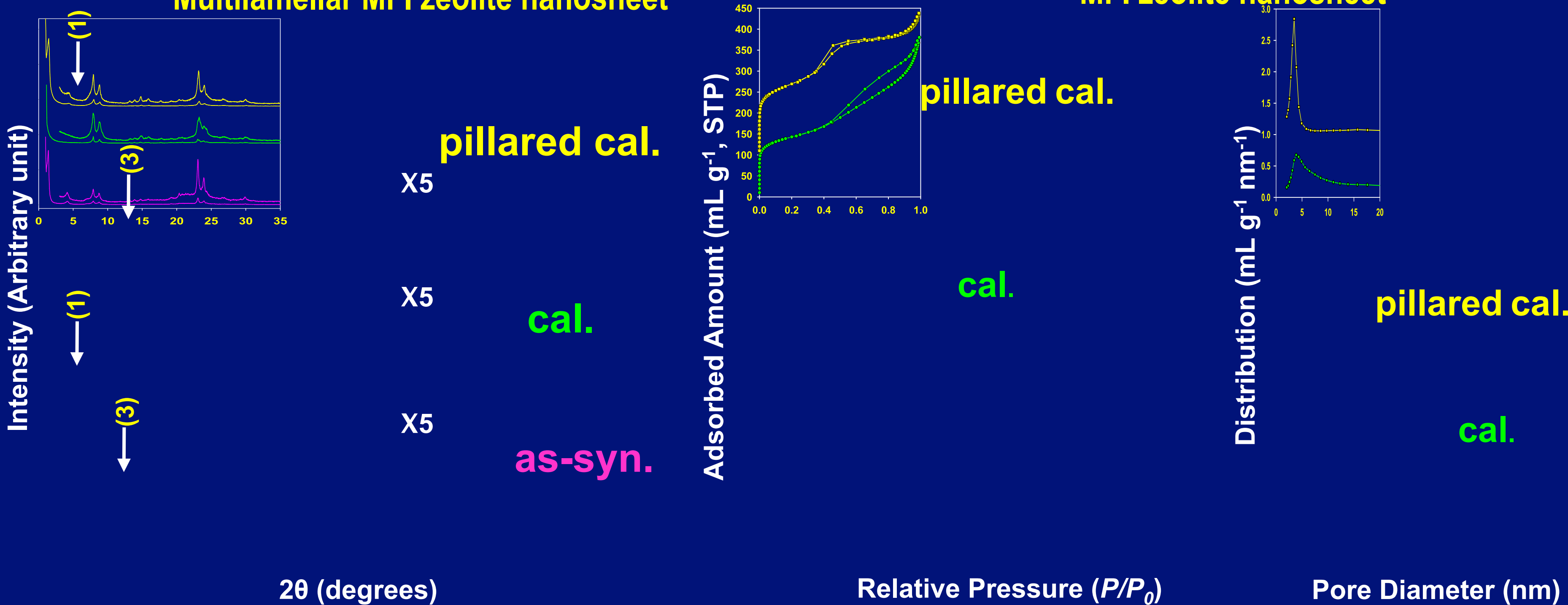
Zeolite MFI Multilamellar Nanosheets



520 m^2g^{-1}, 0.4 cm^3g^{-1}

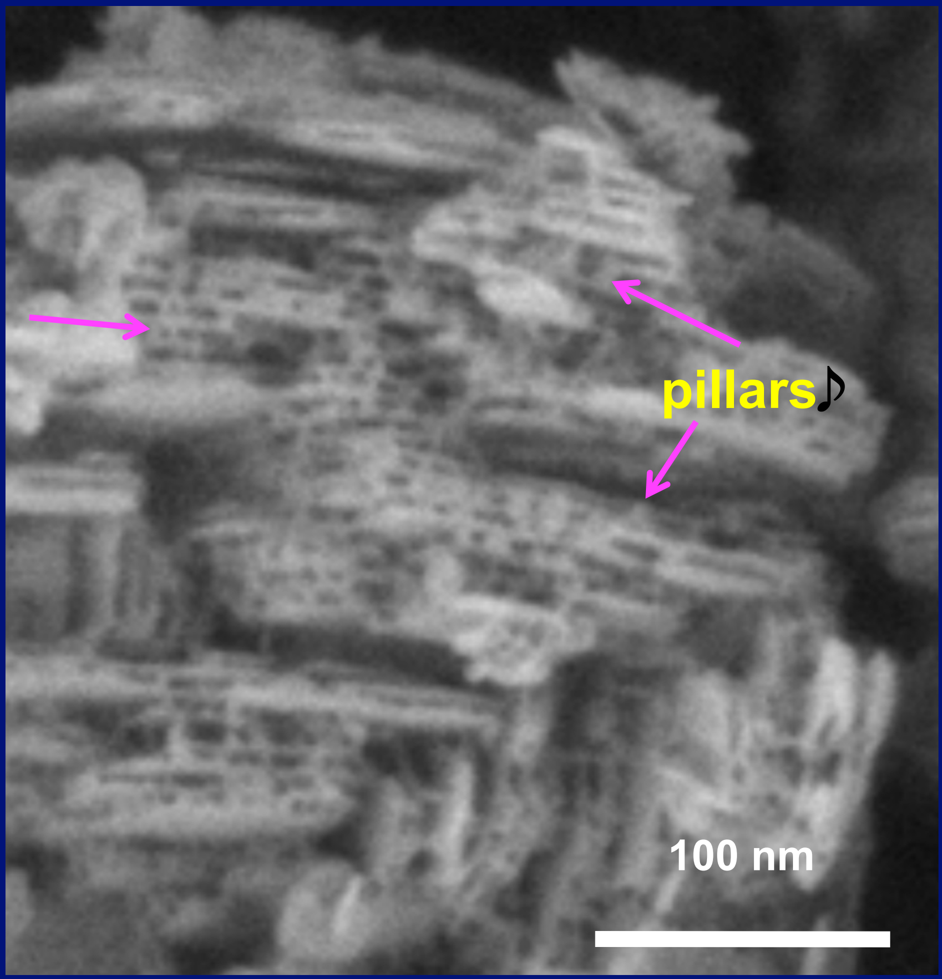
Pillared Multilamellar MFI Zeolite Nanosheets



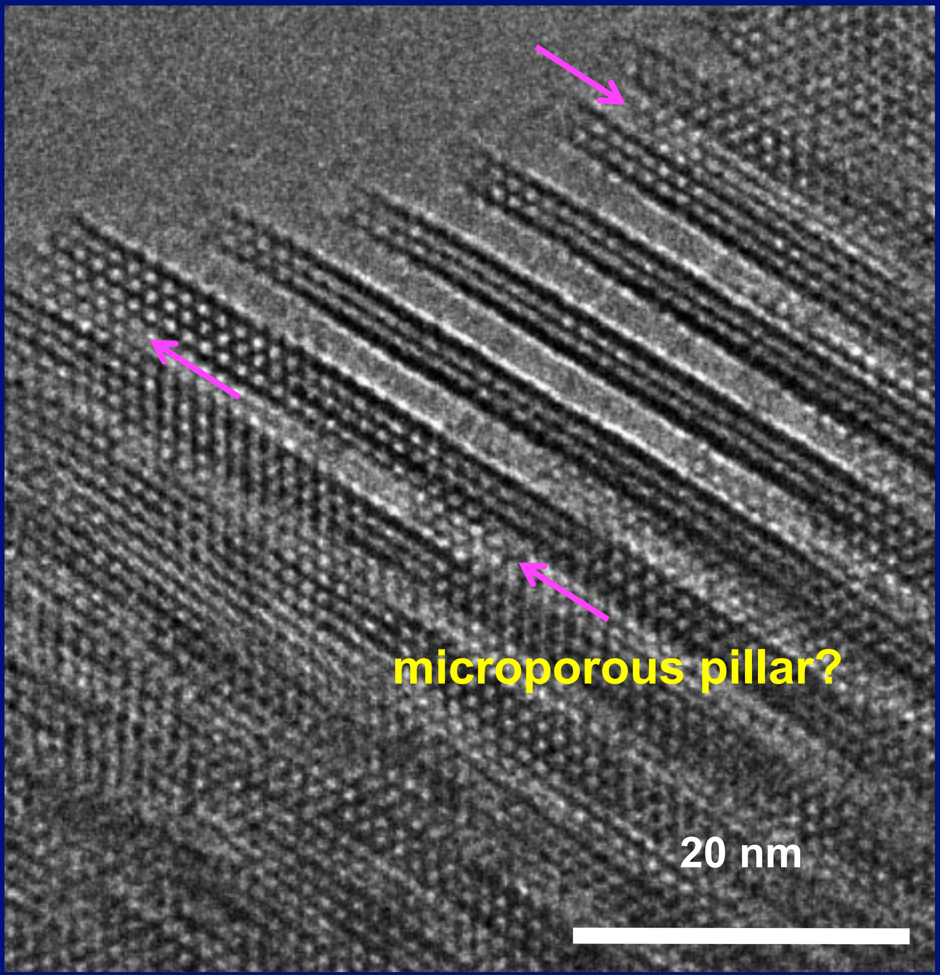


Kyungsu Na et. al. *J. Am. Chem. Soc.* **132**, 4169 (2010)

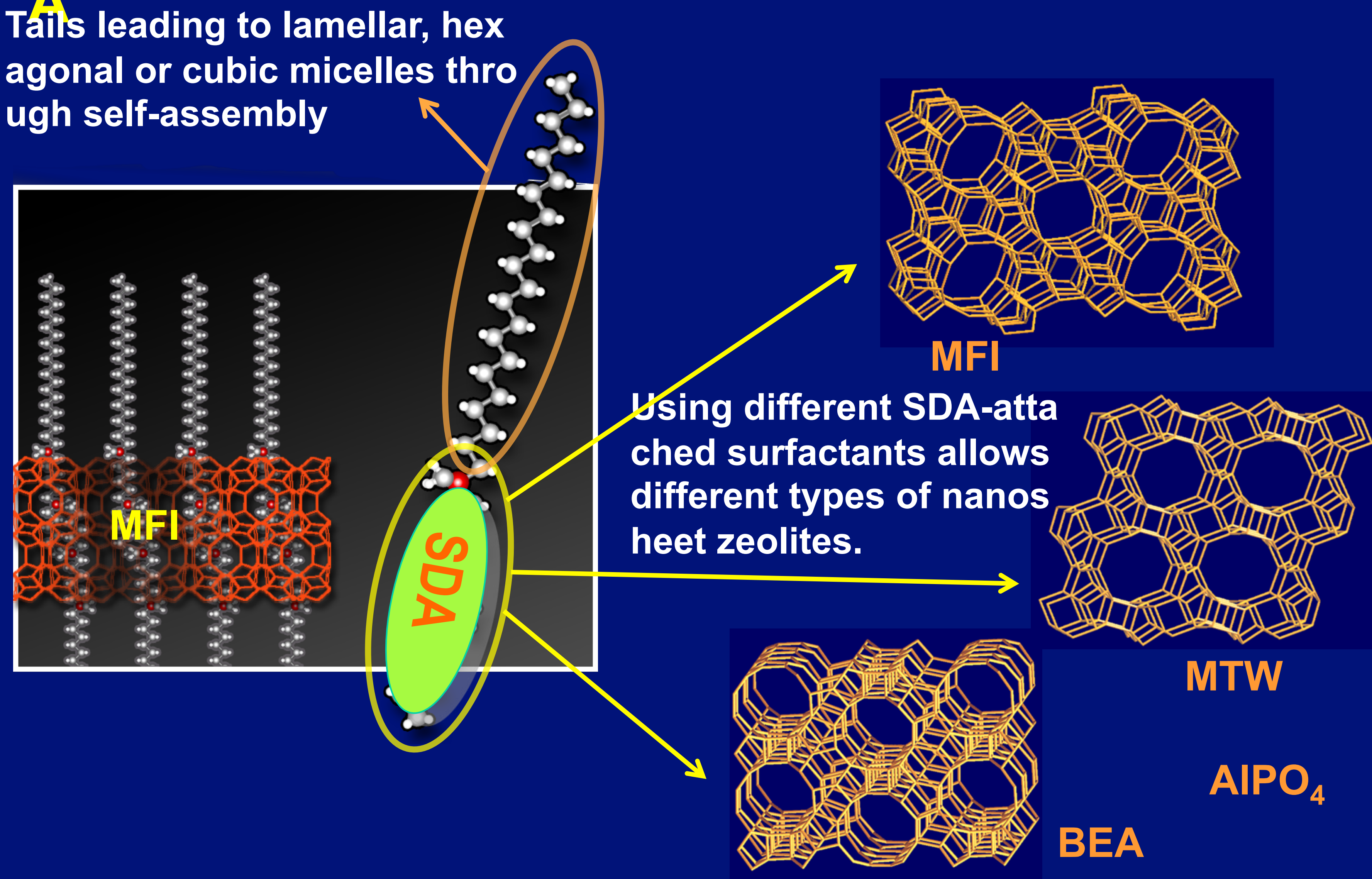
SEM



TEM

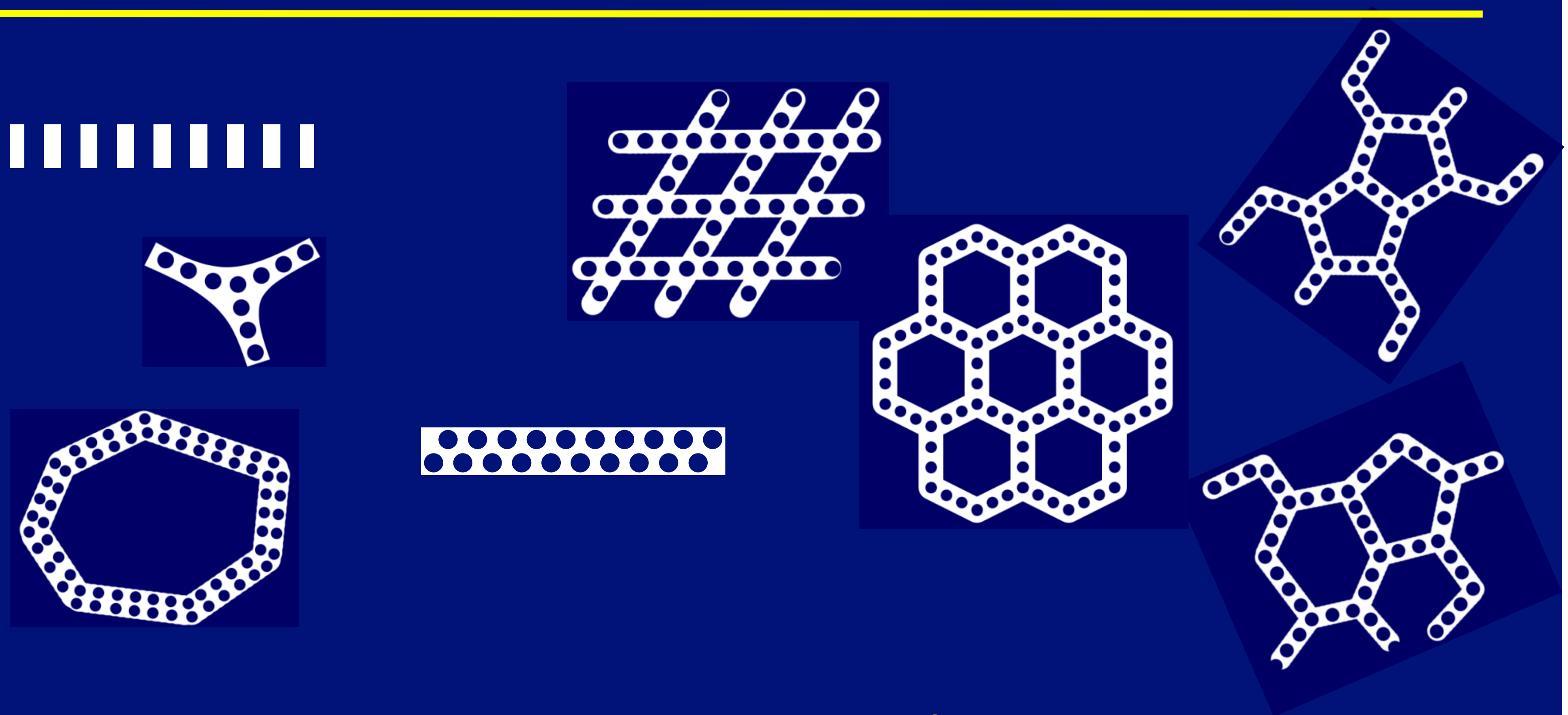


The surfactant head is a structure directing agent (SDA) of zeolite while the tail is a mesopore SDA



Outlook

Synthesis of new zeolitic materials can be expected

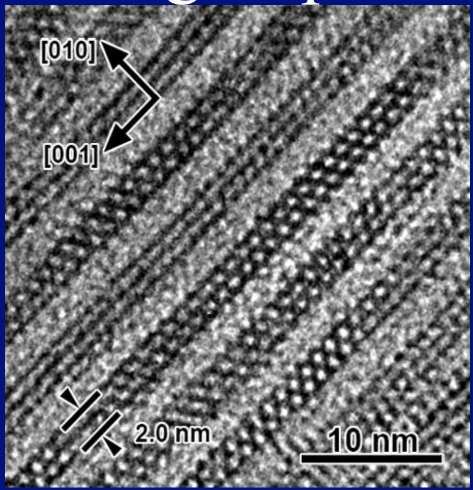


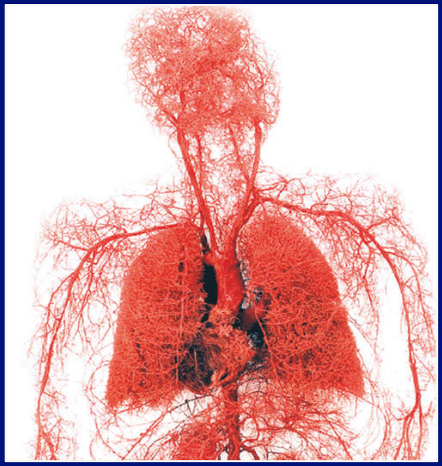
Zeolites with nanoscale morphologies (or nanomorphous ze olites) can be synthesized using a large molecule that conta ins a zeolite-SD functional group.

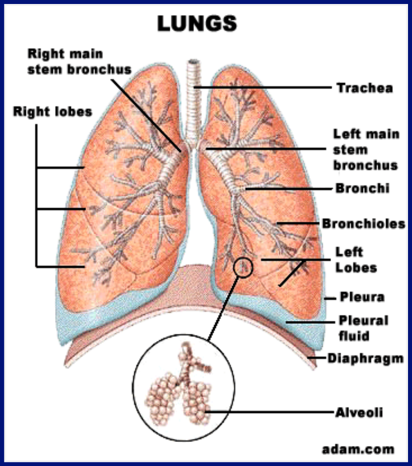
Hierarchically porous zeolite structure is useful fo r design of high performance catalysts

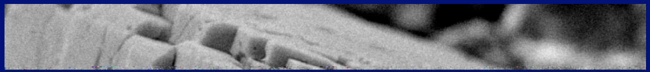
‘To maximize function in a limited space’

- facile transport, maximum density of functional groups



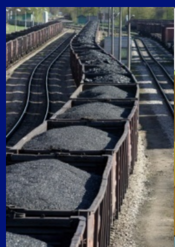
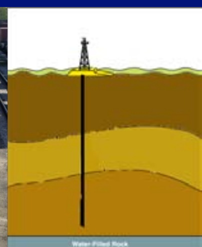






200 nm

Methanol-to-Hydrocarbon Conversion over MFI

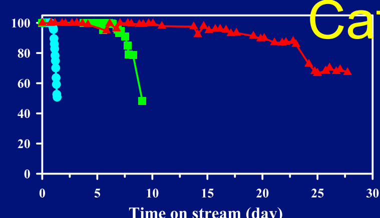



Coal — Natural gas → Synthesis gas $CO + H_2$ → Methanol → MTH Technology

Methanol
↳ Dimethylether + water
→ **Zeolite catalyst** → Olefin/ Gasoline

Gasoline

Catalyst deactivation

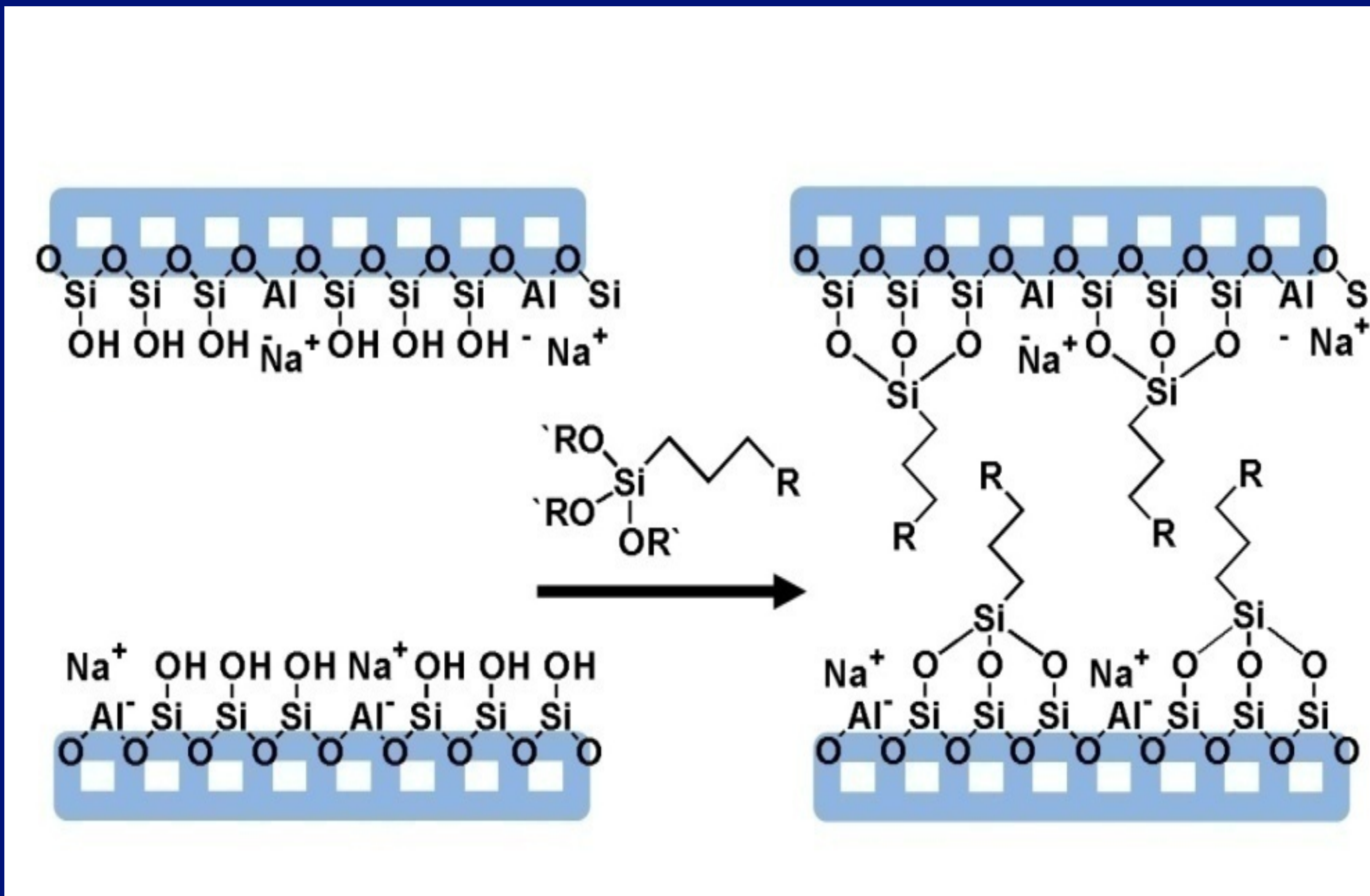


ZSM-5 Si/Al=15 — ZSM-5 Si/Al=41 — Unilamellar MFI Si/Al=53

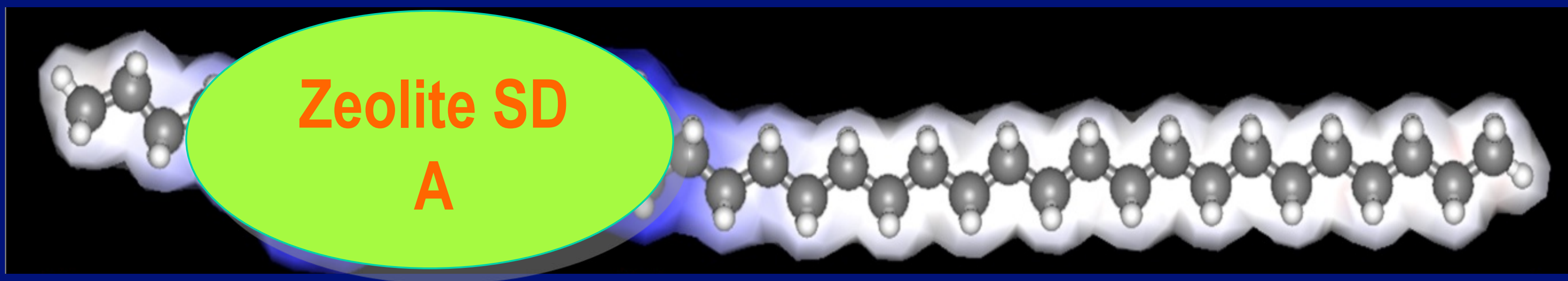
Selectivity

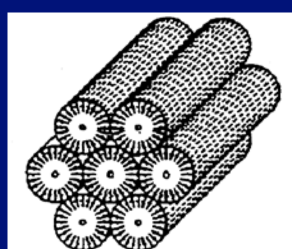
	Olefins	Gasoline	Others
ZSM-5 (15)	15	56	29
ZSM-5 (41)	32	46	22
Unilamellar MFI (53)	36	43	21

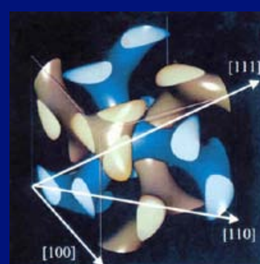
Organic-functionalization of zeolite mesopore walls is possible

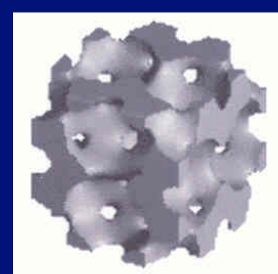


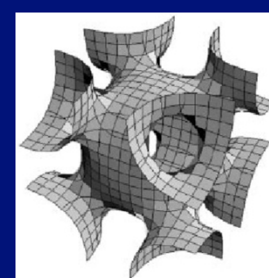
Conclusion: It is possible to synthesize mesoporous materials using a surfactant that is functionalized with a zeolite structure directing agent .

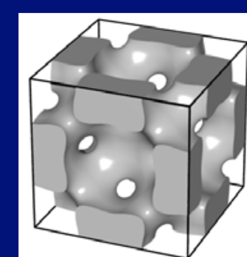












These ordered structures would be possible to synthesis wit
h crystalline zeolite frameworks in the near future.

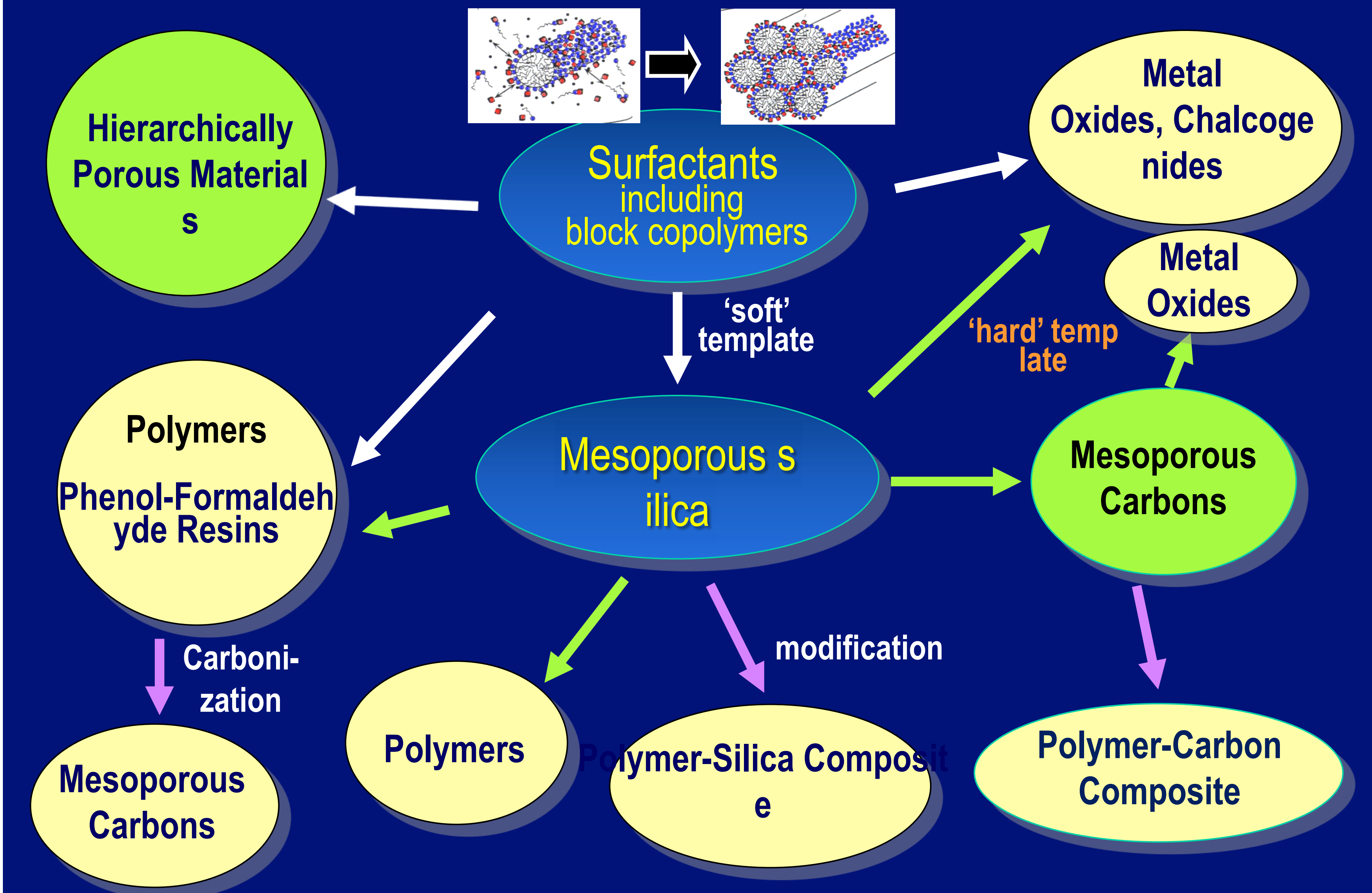
The mesopore diameters are controllable. The wall thi ckness is also adjustable within a certain range.

What is the mechamism for the formation of extremely thin zeolite crystals?
Is it different from bulk crystallization?

The synthesis strategy using functionalized surfactant would be applied to materials other than silica or alumi nosilicate.

These new zeolitic materials would provide many new opportunities for researches and applications.

Various Materials Available via Surfactant-Assembling Route and Hard-Templating Route



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