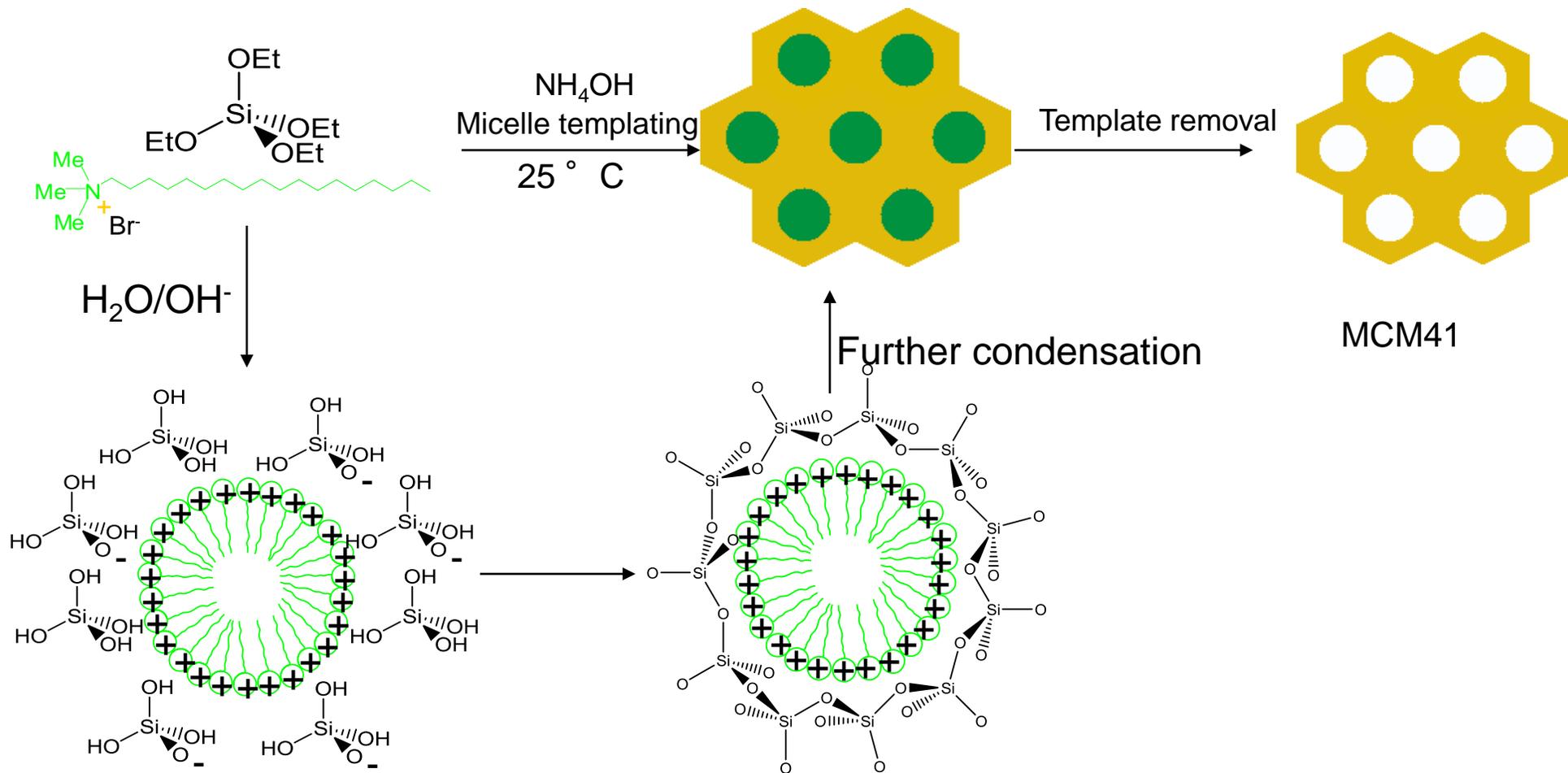


New directions in  
High-pressure Chemistry  
with  
Periodic Mesosstructured Materials

Efree2 talk, Oct 22, 2014

# Discovery of Periodic Mesoporous Silicas

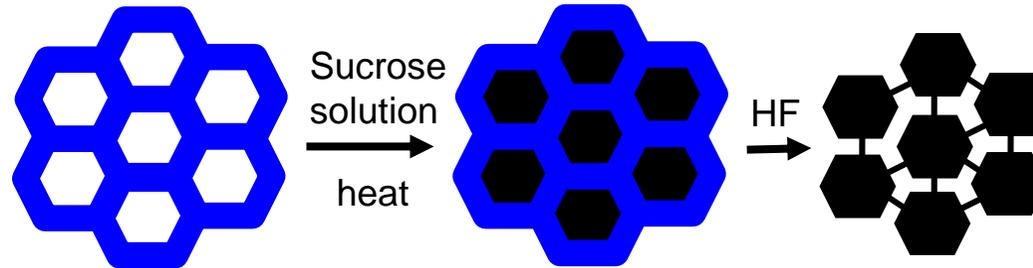
Kresge, C. T., Leonowicz, M., Roth, W. J., Vartuli, J. C. & Beck, J. C. *Nature* **359**, 710-712 (1992).



Periodic mesoporous silicas have ordered mesopores (2-50 nm) in a silica framework.

# Nanocasting as templating strategy

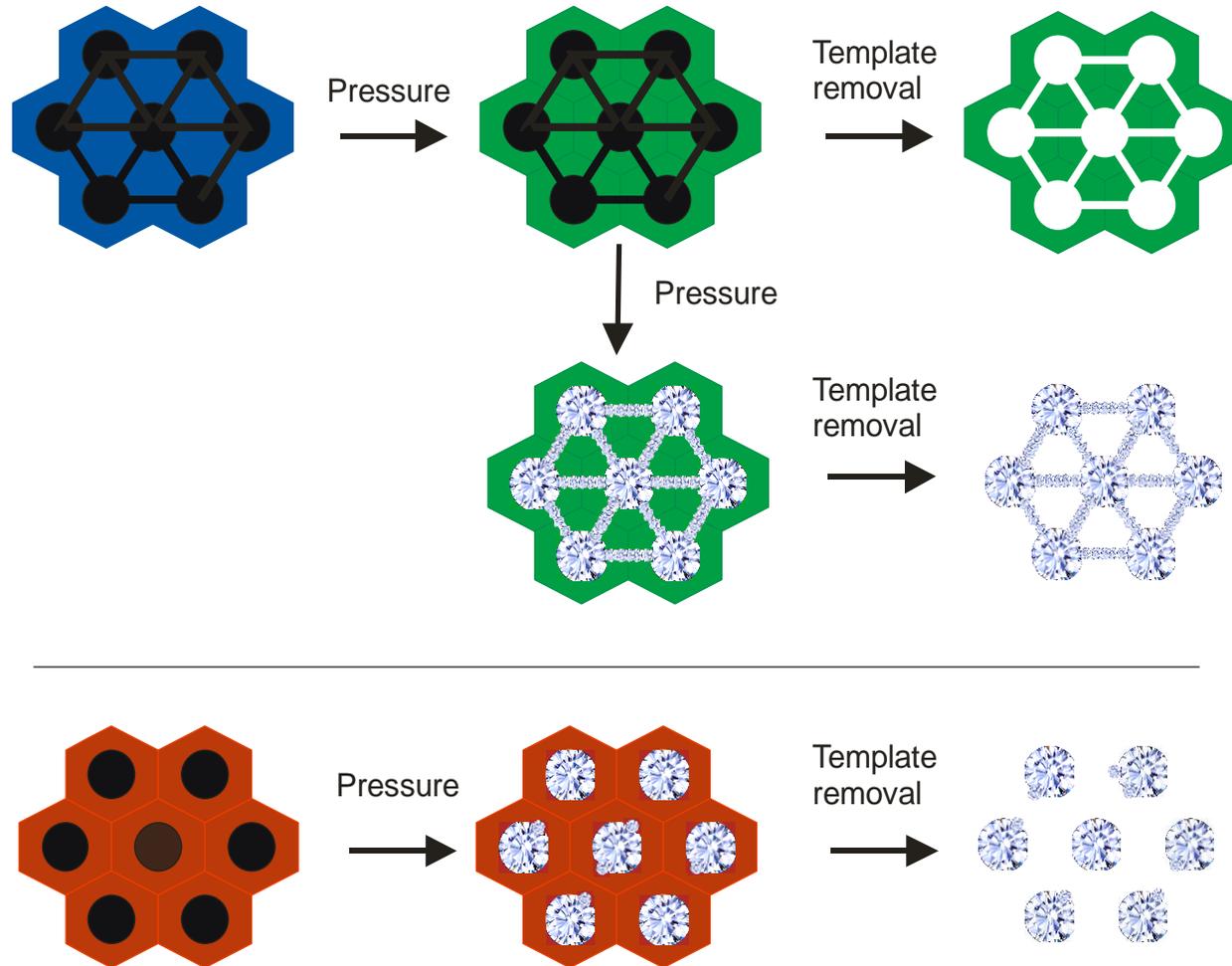
Use of periodic mesoporous silica, e.g. SBA-15 as template.



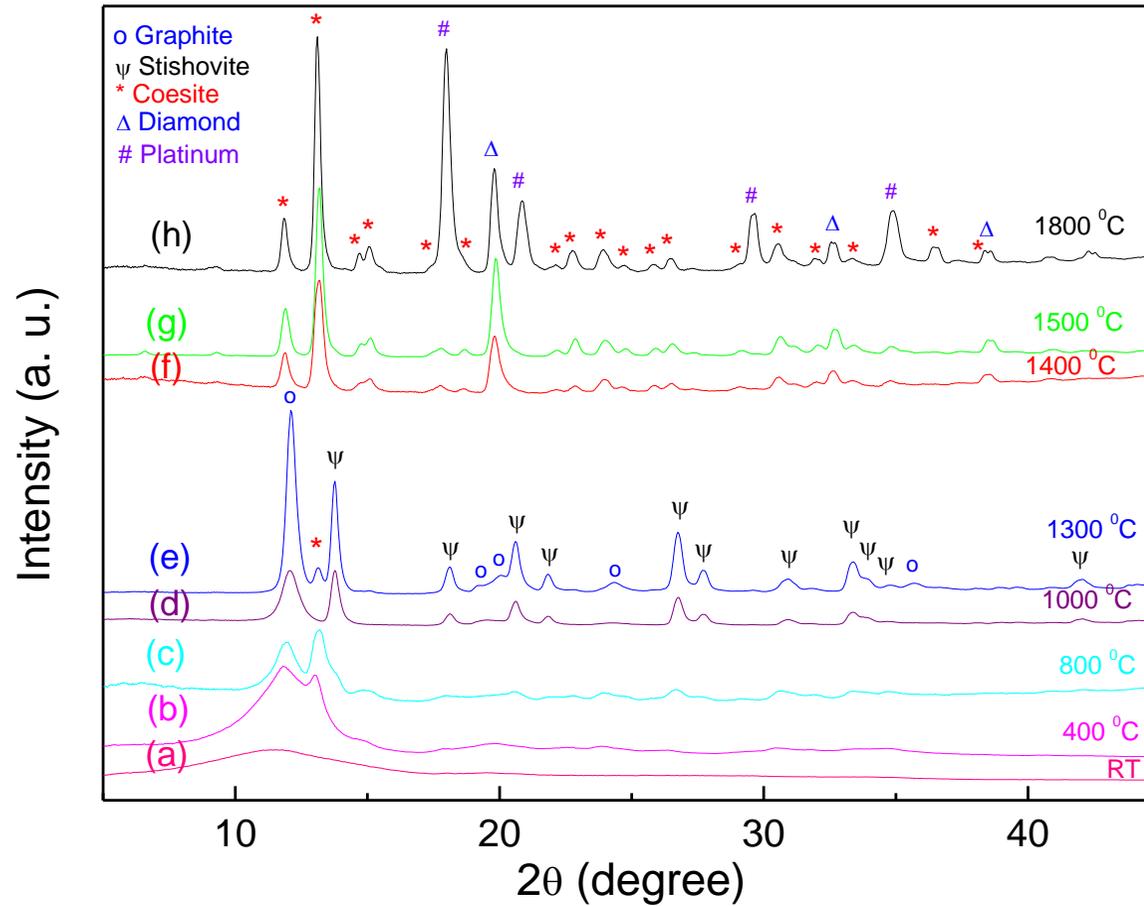
R. Ryoo et. al. *J. Phys. Chem. B* **1999**, 103, 7743.

- Materials like nitrides and metals which can't be synthesized in an aqueous medium may be produced by nanocasting.
- Control over the pore system i.e., hexagonal or cubic etc.

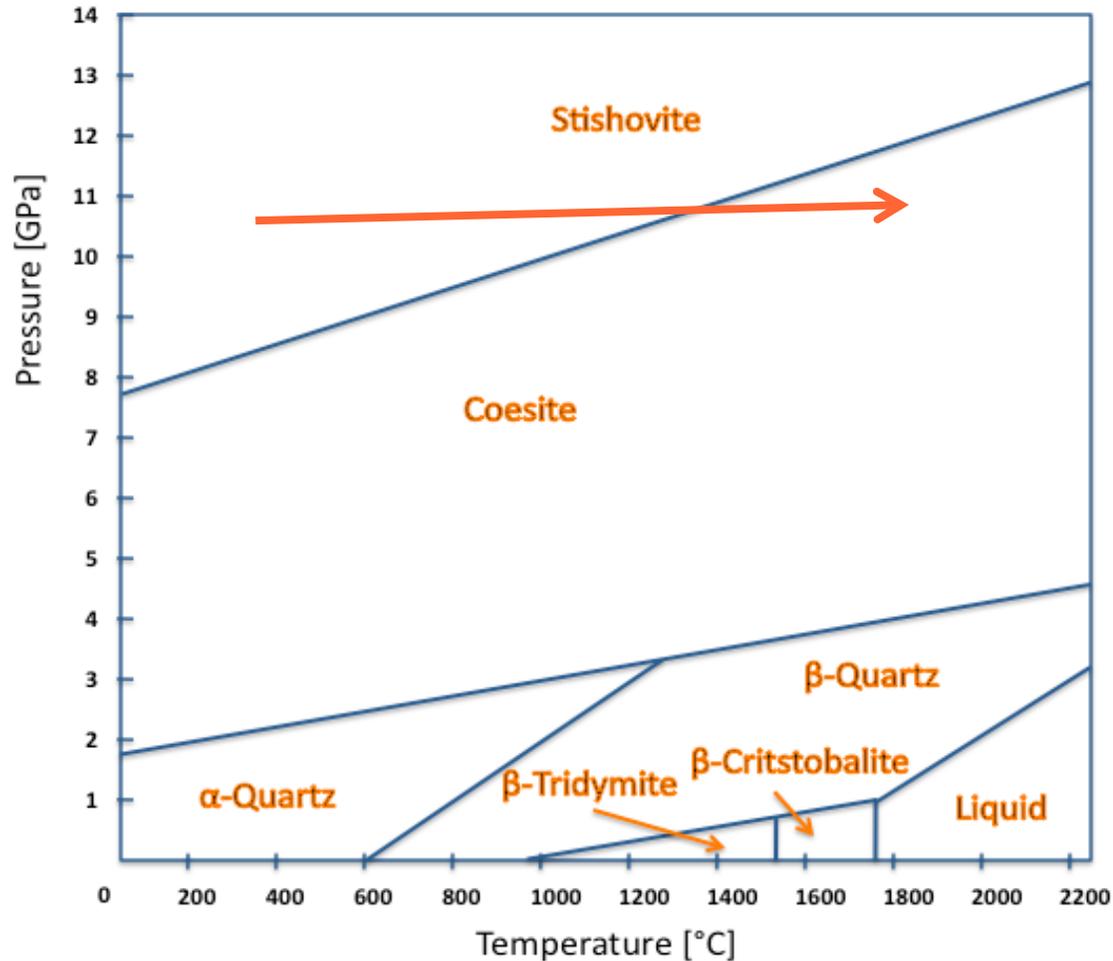
# Nanocasting at high pressure



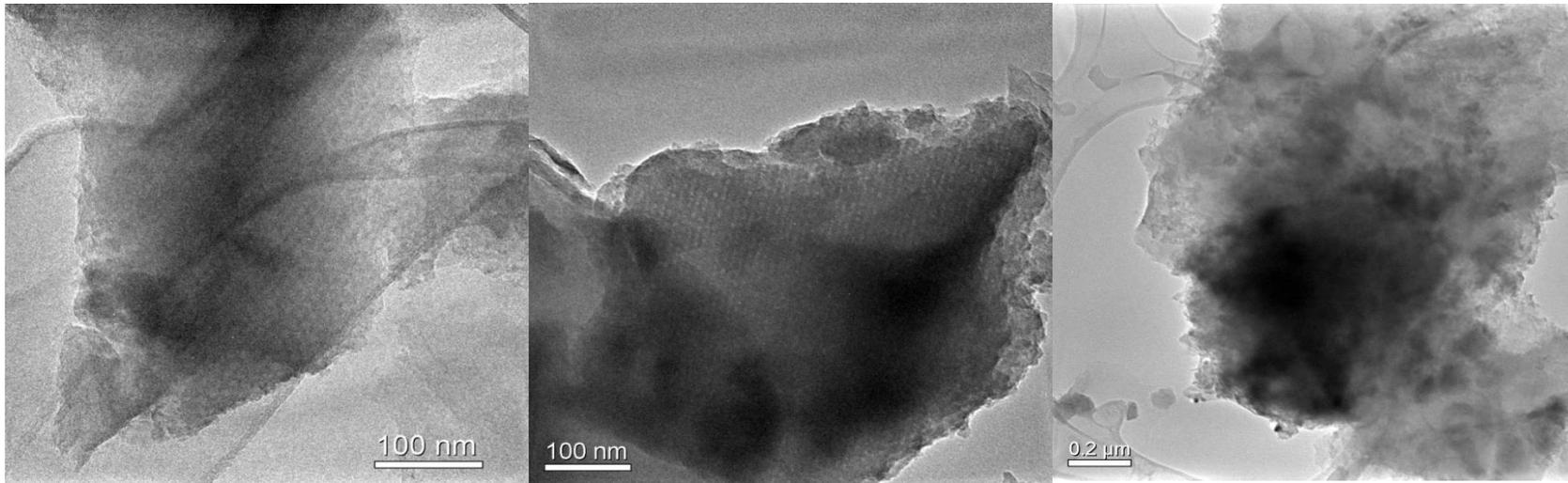
# SBA16/Carbon composites at 10 GPa



# Phase diagram of silica



# SBA16/C composites at 10 GPa

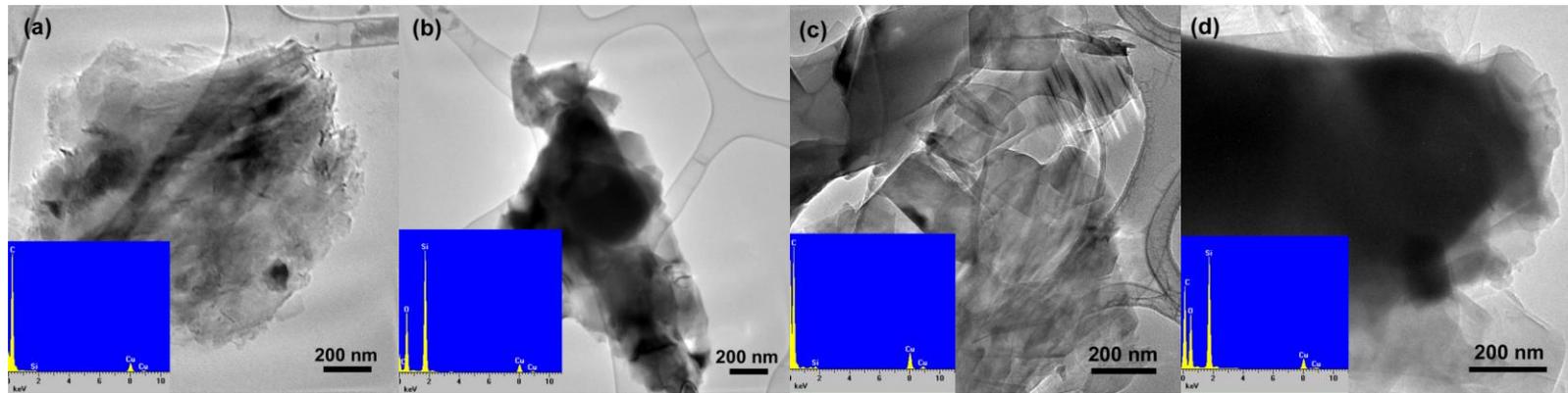


RT

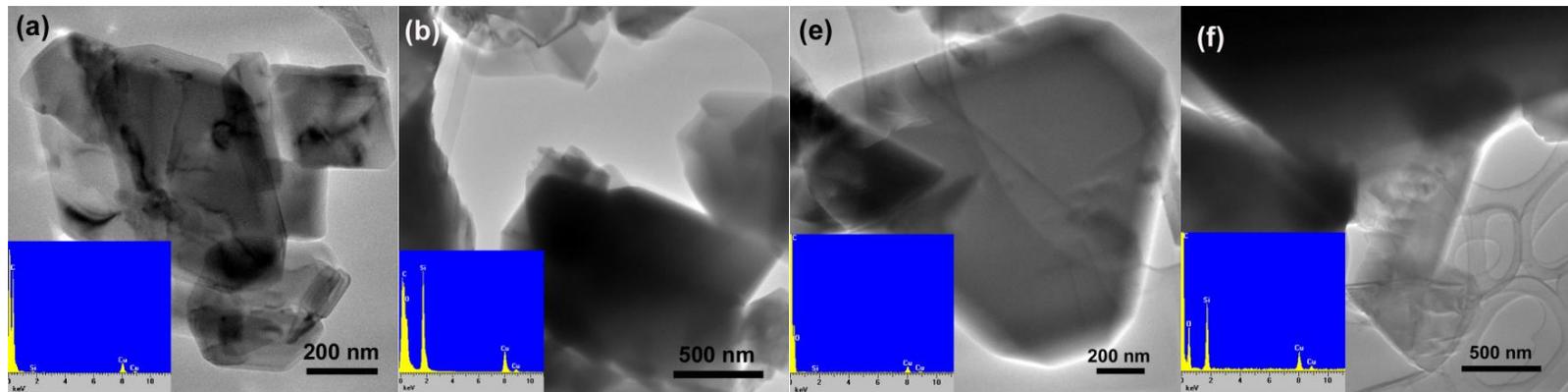
400 ° C

800 ° C

# SBA16/C composites at 10 GPa



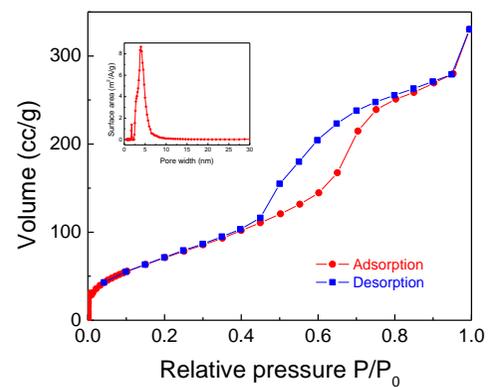
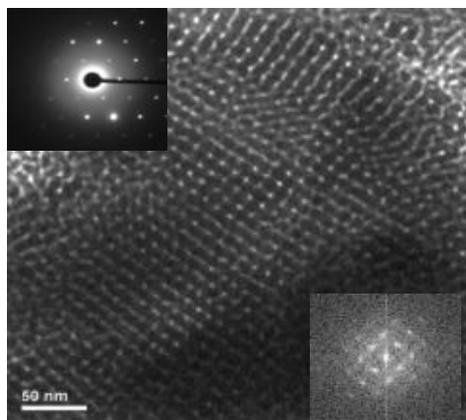
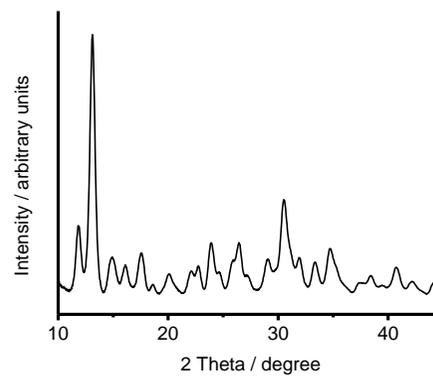
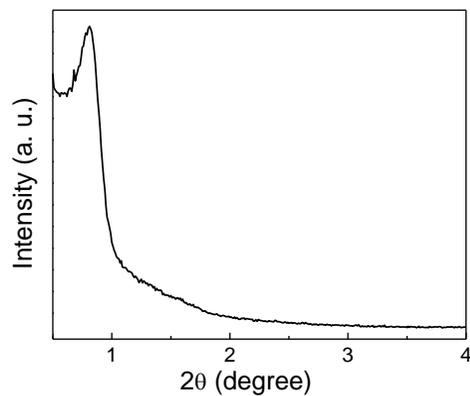
1000 ° C



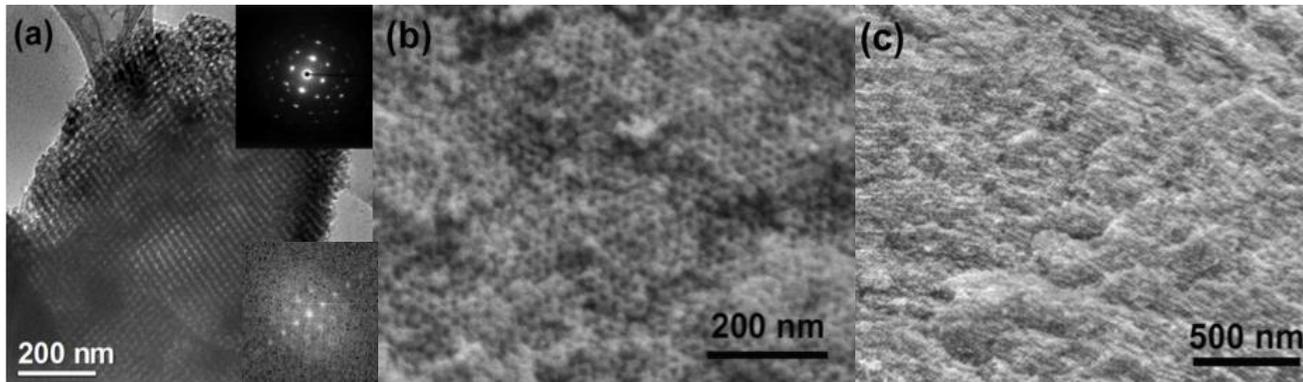
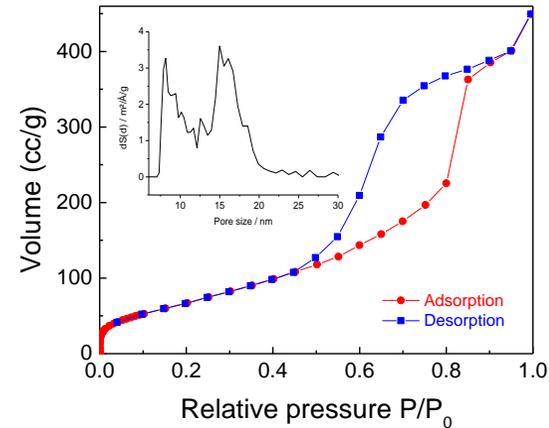
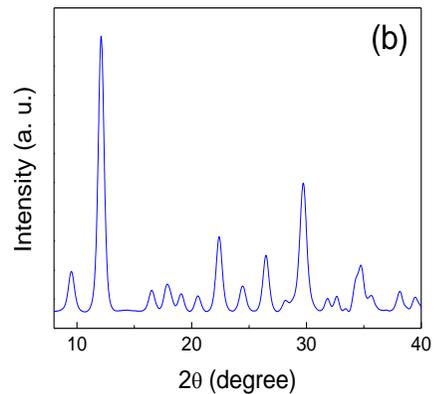
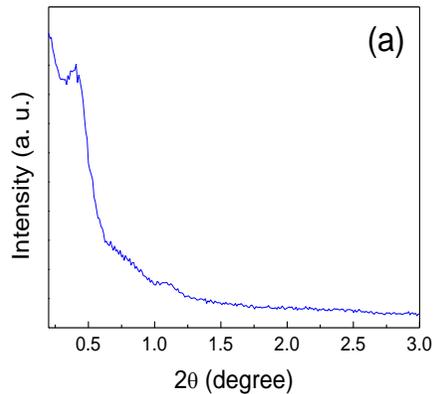
1400 ° C

1800 ° C

# Periodic Mesoporous Coesite



# Large-pore periodic mesoporous quartz



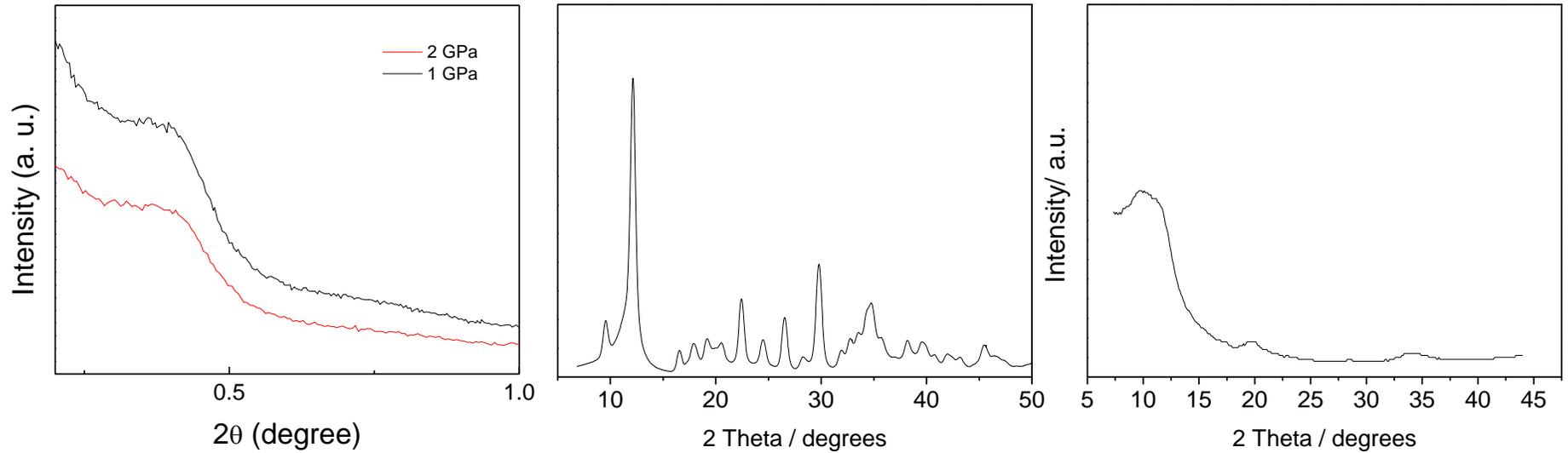
Starting material: Large-pore FDU-12 (fcc lattice of spherical mesopores (19 nm size))

Synthesis conditions: 4 GPa, 750 ° C

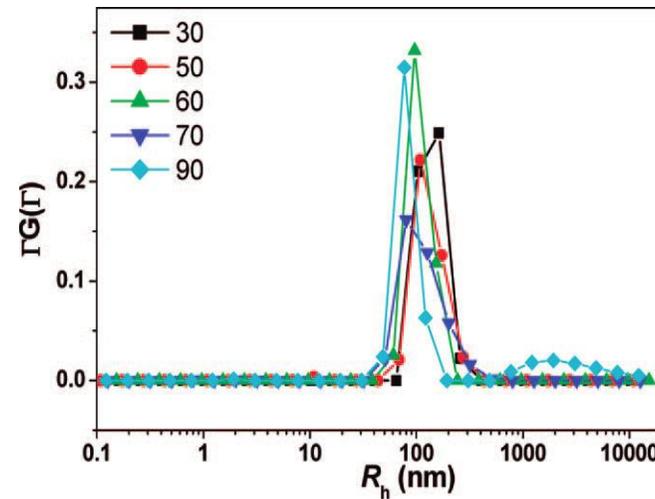
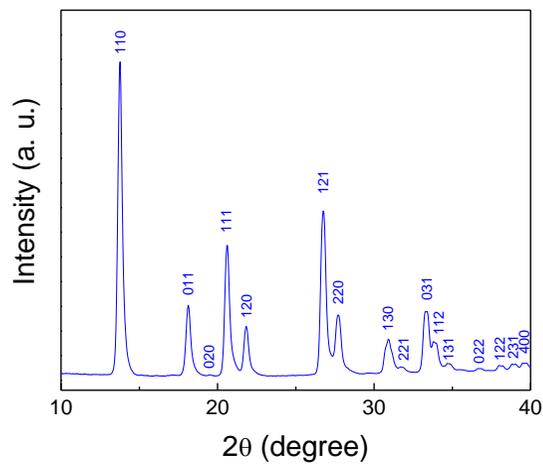
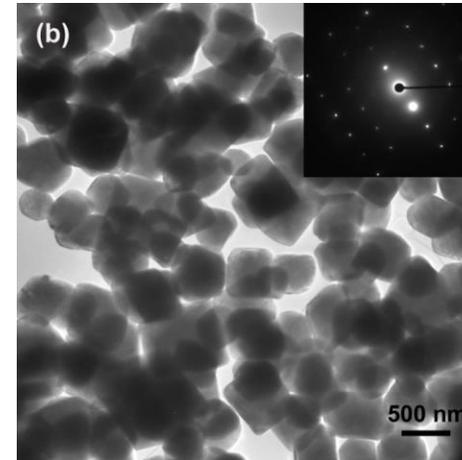
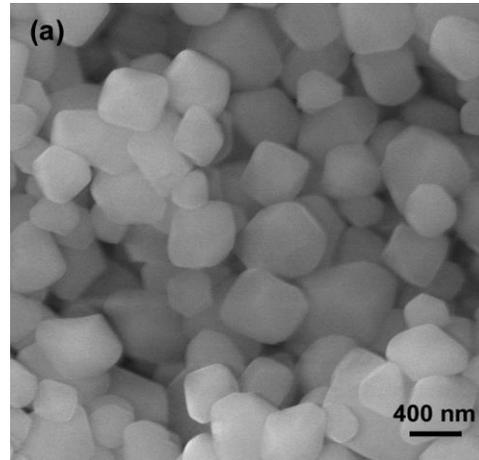
Surface area 238 m<sup>2</sup> g<sup>-1</sup>

Lattice parameter  $a = 39$  nm

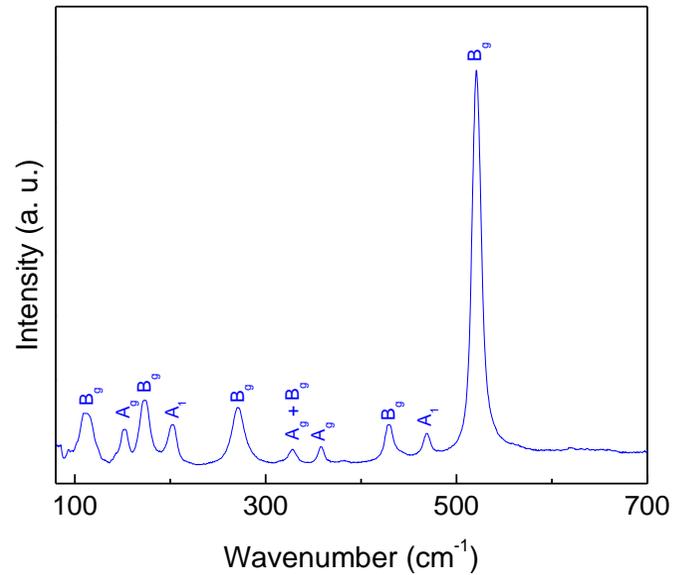
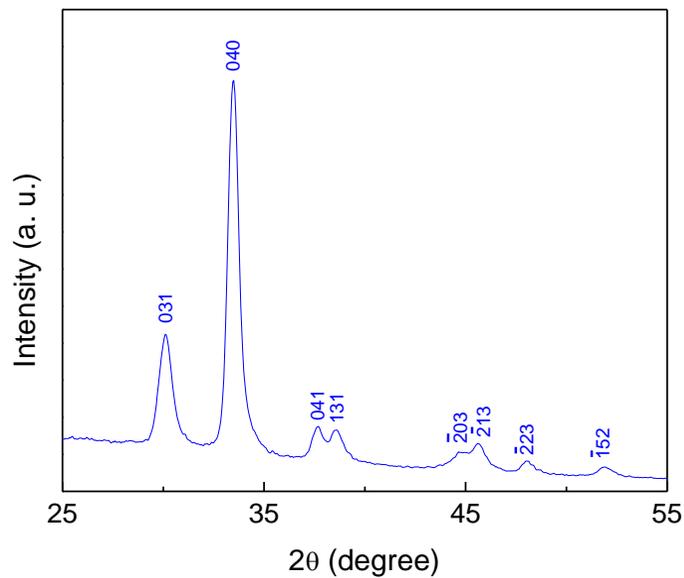
# Synthesis at 1 and 2 GPa at 750 ° C



# Stishovite Nanocrystals from SBA-16 (12GPa, 400° C)

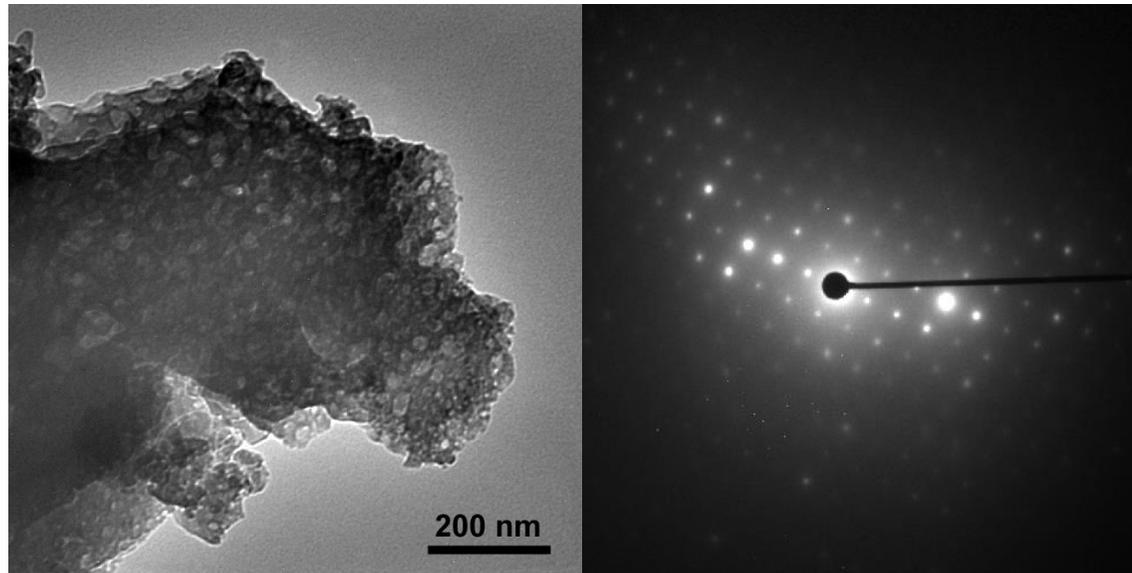


# What happens below 400 ° C?

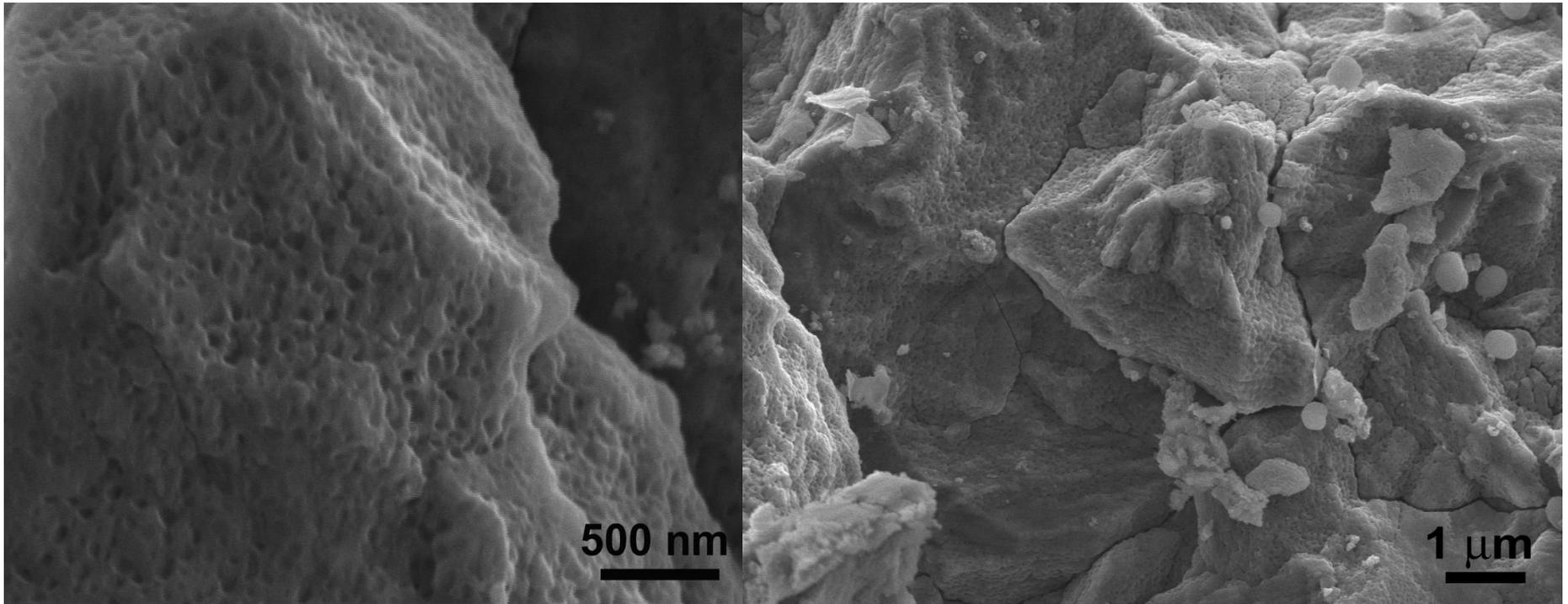


PXRD and Raman spectrum of SBA-16 at 12 GPa and 300 ° C

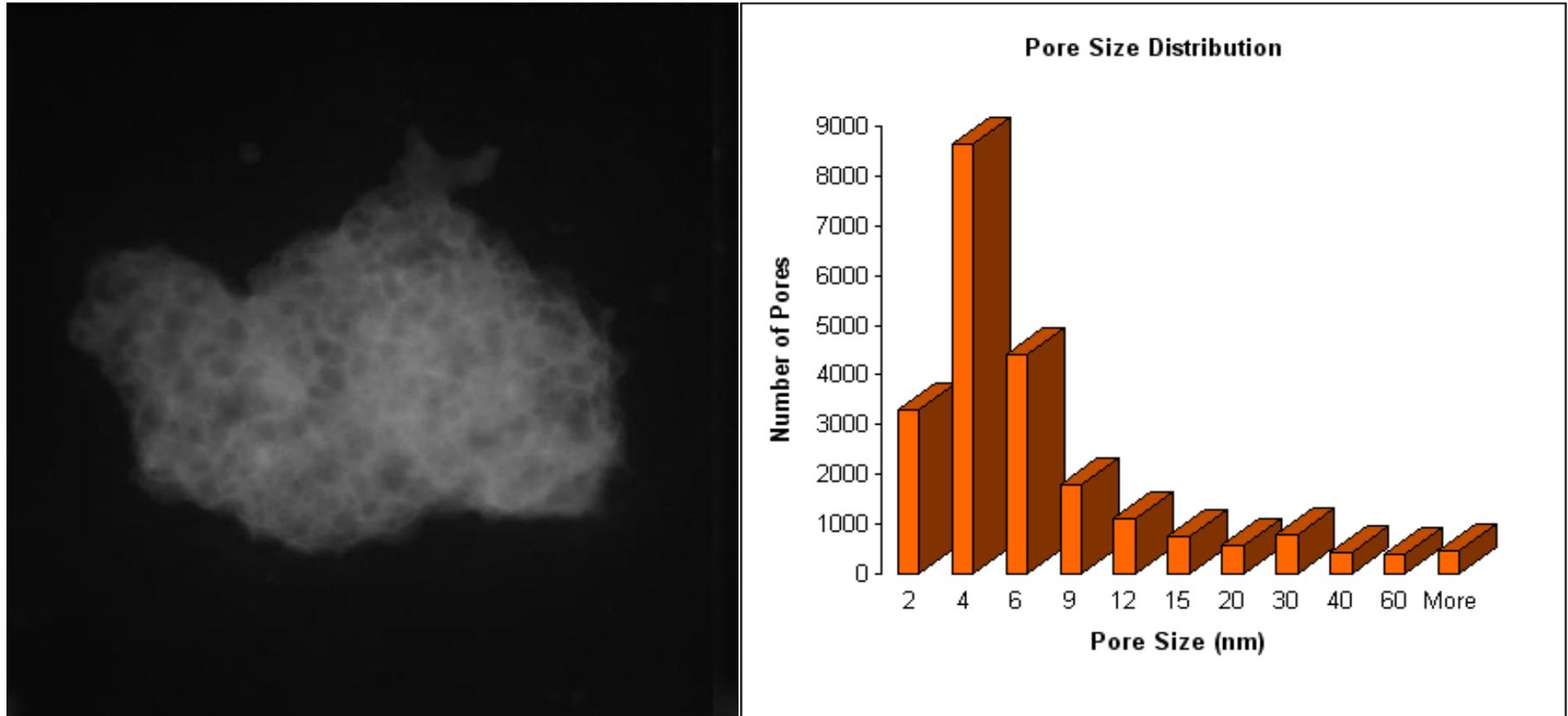
# Direct formation of mesoporous coesite single crystals from SBA-16



# Direct formation of mesoporous coesite single crystals from SBA-16

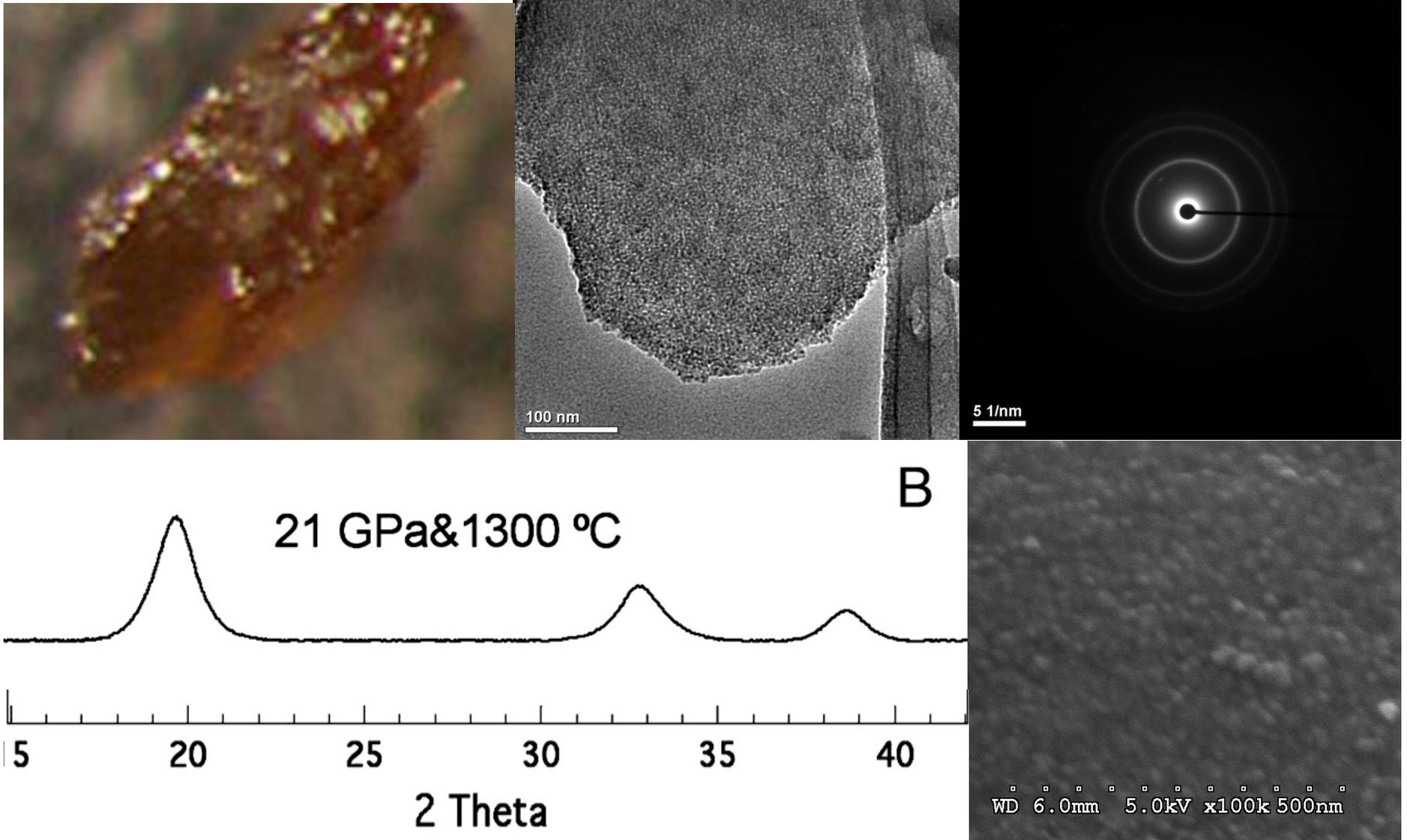


# 3D-STEM analysis

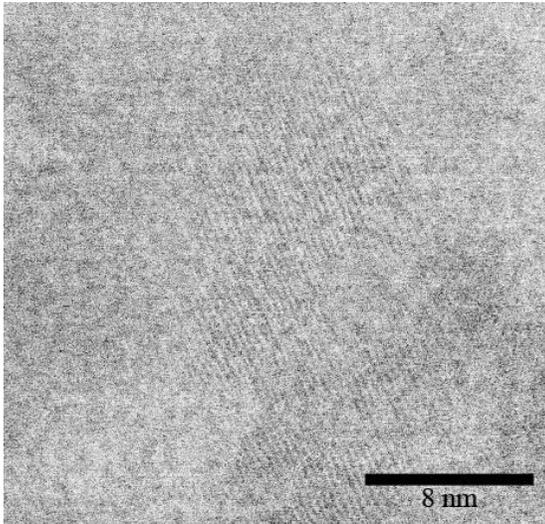


Estimated Porosity:  $49 \pm 9 \%$   
Estimated Surface area:  $54 \text{ m}^2 \text{ g}^{-1}$

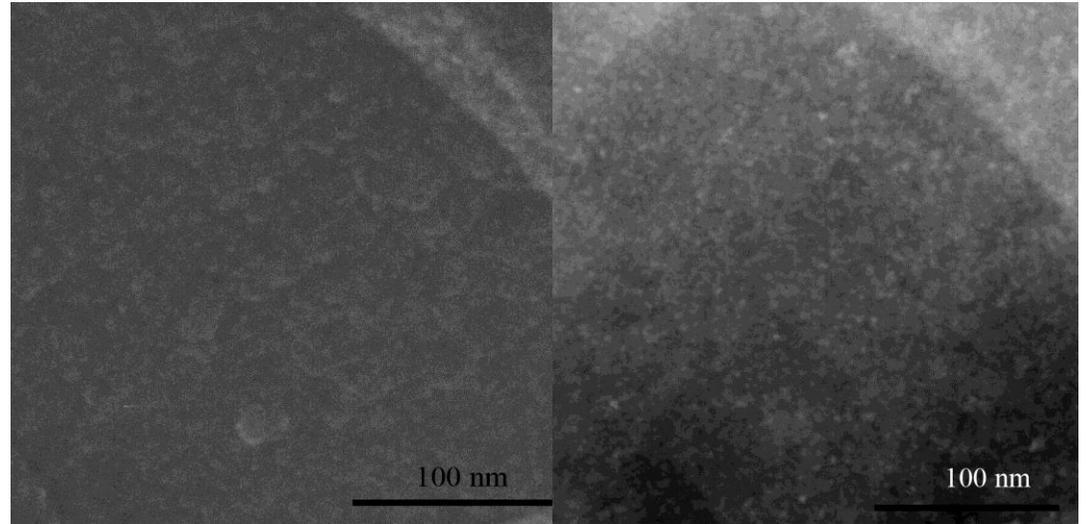
# Diamond from periodic mesoporous carbon CMK-8



# Diamond from periodic mesoporous carbon CMK-8

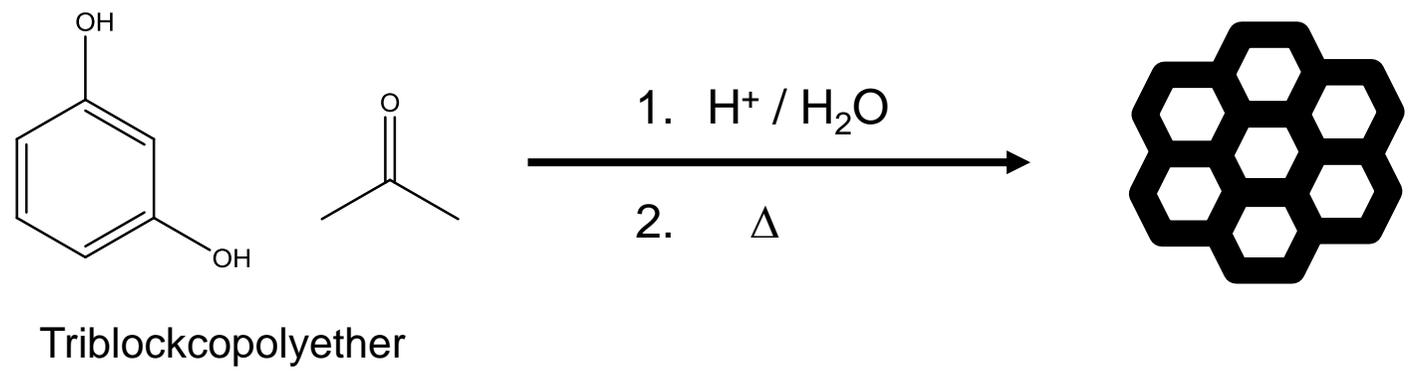
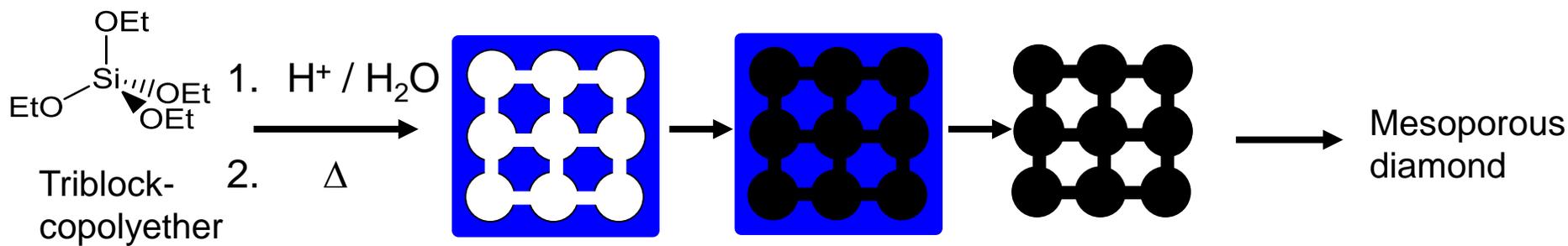


HR-TEM

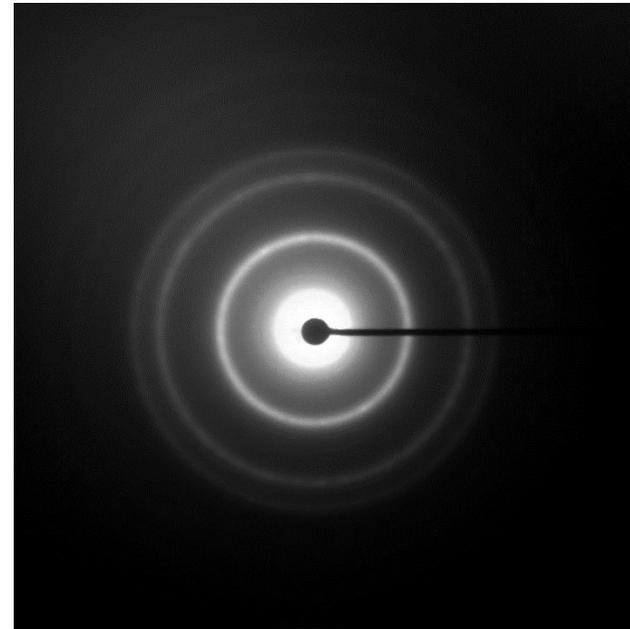
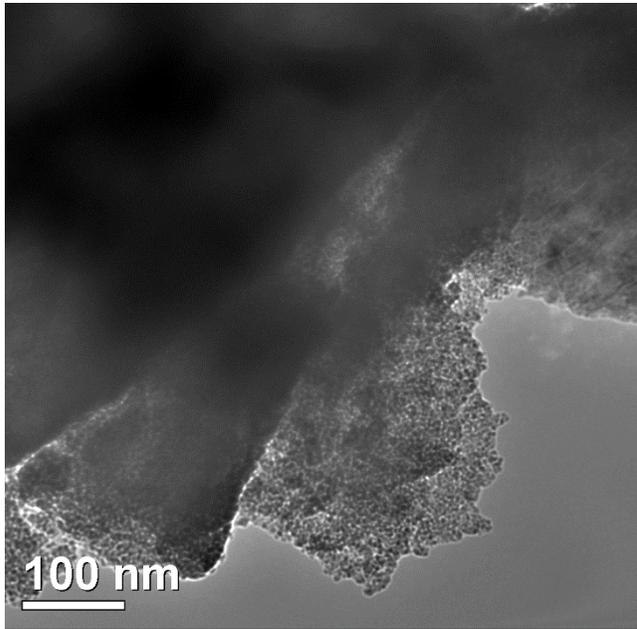


SEM and Z-contrast HAADF-TEM

# Mesoporous diamond from hexagonal soft-self-assembled carbon

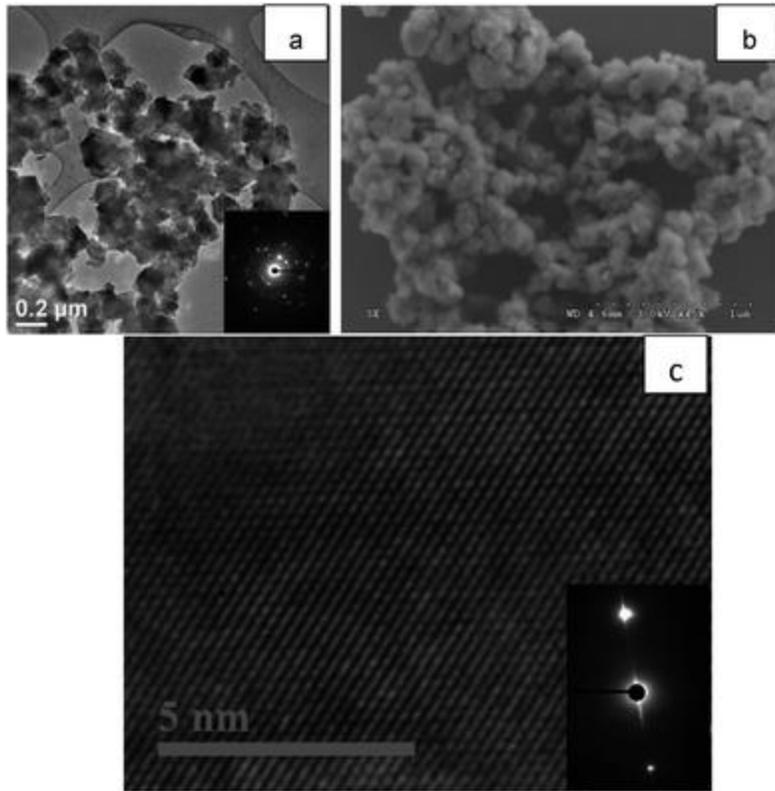


# Diamond synthesis from soft-self-assembled SBA-15 type carbon

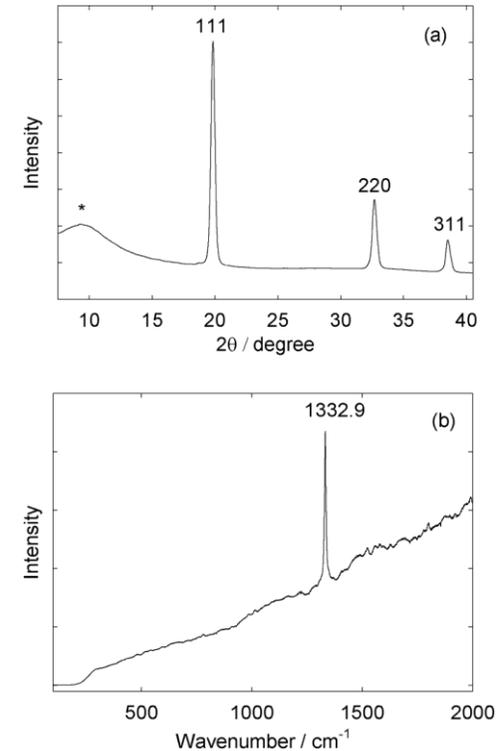


Synthesis conditions: 21 GPa, 1300 °C.

# Diamond synthesis from soft-self-assembled SBA-15 type carbon at 14 GPa

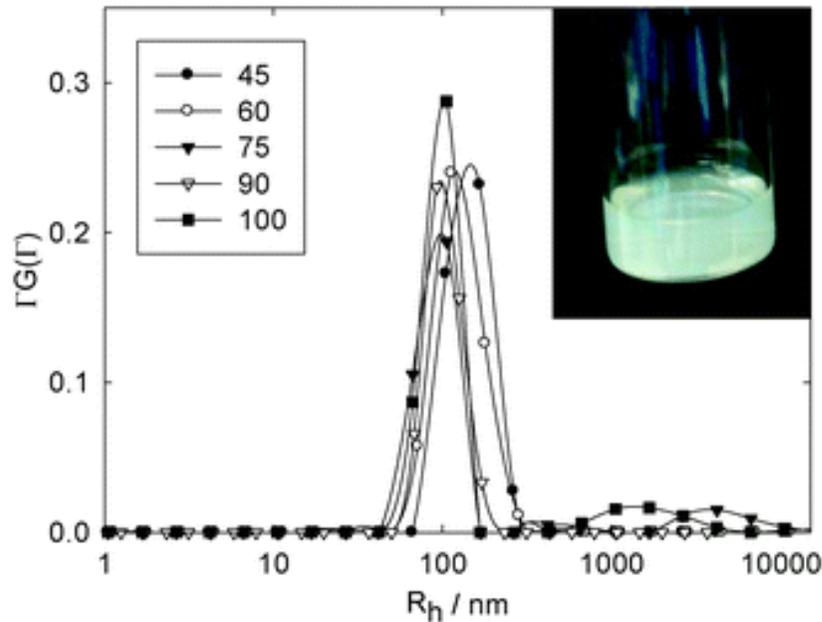


(a) TEM image and SAED pattern (inset of a), (b) SEM image, and (c) HR-TEM image and SAED pattern (inset of c) of diamond nanocrystals synthesized at 14 GPa/1300 ° C.



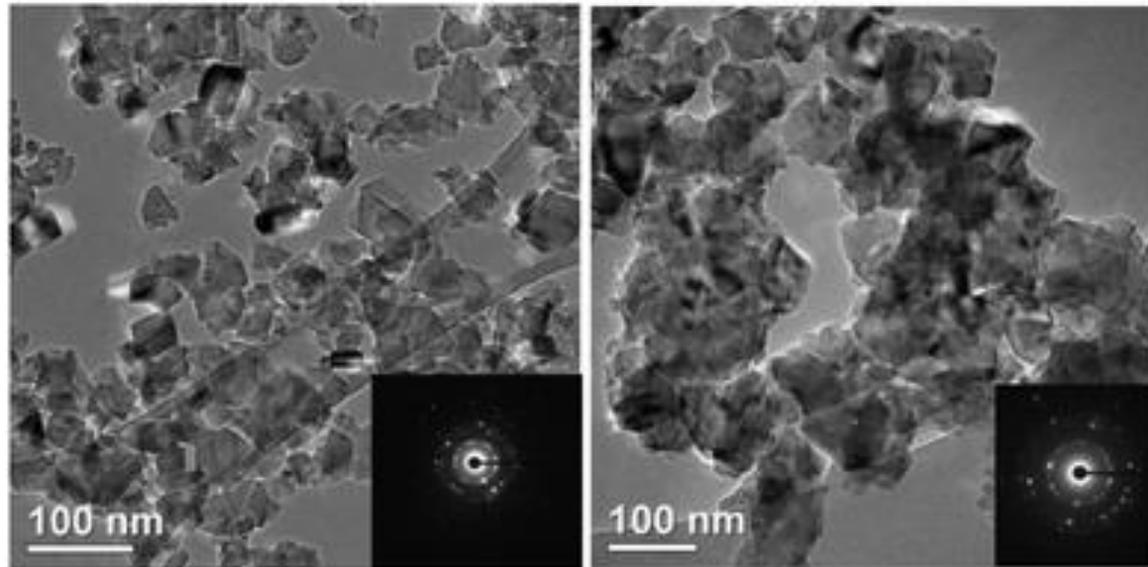
(a) XRD pattern (Mo Kα) and (b) the UV-Raman (λ<sub>ex</sub> = 325 nm) spectrum of synthesized diamond nanocrystals. (c) Asterisk (\*) in (a) indicates amorphous carbon.

# Diamond synthesis from soft-self-assembled SBA-15 type carbon at 14 GPa



CONTIN analysis of dynamic light scattering measurements at different scattering angles (45 to 100 degrees) of diamond nanocrystals dispersed in acetone (inset shows diamond solution)

# Diamond synthesis from soft-self-assembled SBA-15 type carbon at 14 GPa



14 GPa, 1400 °C 30 min

14 GPa, 3h, 1400 °C.

50 nm crystals

200 nm crystals

Lowering the pressure to 12 GPa, 1300 °C only yielded graphite.

# Future directions

- At which pressure is the transition between the diamond nanocrystals and the mesoporous diamond?
- What are basic physical properties like the thermal conductivity and the hardness of mesoporous diamond compared to other porous materials?

# Future directions

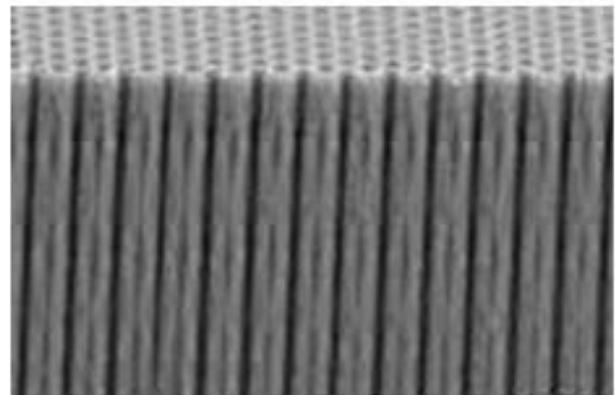
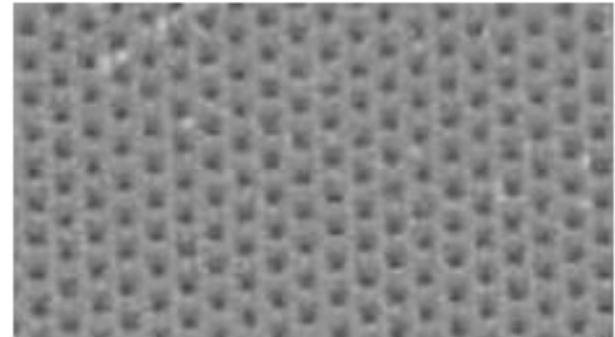
How can we still realize nanocasting of diamond structures?

- Extend lattice parameters (pore and pore wall diameter).
- Switch to a more inert template that does not make phase transitions.
- Choose a one-dimensional pore system to reduce dependency on periodicity.  
→ Diamond nanofibers

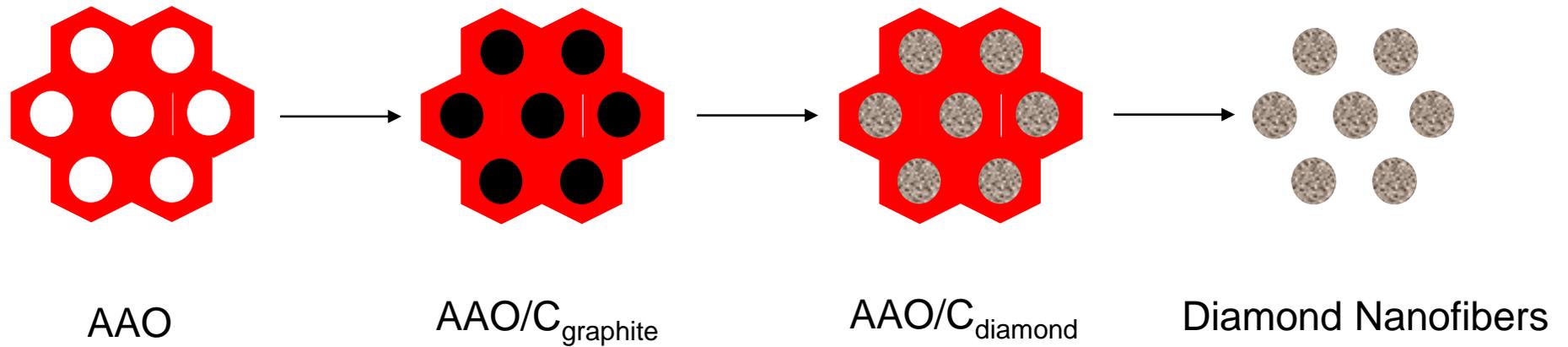
# Bulk synthesis of diamond nanofibers

Anodic aluminum oxide (AAO) as template:<sup>1</sup>

- $\text{Al}_2\text{O}_3$  is more inert than silica.
- $\text{Al}_2\text{O}_3$  does not make phase transitions at high pressure.
- Pore walls and pore sizes are highly tunable (ca. 20-200 nm).
- AAO has strictly one-dimensional, non-interconnected channels.
- Template can be removed in strong base.



# Bulk synthesis of diamond nanofibers



# Bulk synthesis of diamond nanofibers

Closed knowledge gaps: We will know how to

- nanocast diamond structures in a high-pressure synthesis.
- produce non-aggregated diamond nanofibers in bulk.
- produce processible diamond nanofibers in bulk.

Energy needs:

- Diamond nanofibers as one-dimensional thermal conductors.
- Diamond nanofibers for reinforced polymers.
  - More facile functionalization compared to carbon nanotubes.
  - More facile integration compared to carbon nanotubes.
  - Smaller loss of transparency in the polymers.

# Scalable, hydrothermal growth of mesoporous quartz single crystals

How can we further decrease pressure and improve scalability?

Conditions:  $T_{\text{diss}} = 375^{\circ}\text{C}$ ;  $T_{\text{growth}} = 350^{\circ}\text{C}$ ,  $P = 9,000\text{ psi}$   
Overall growth time: 5 days



Quartz seed crystal plate  
before growth

12.8 mm (X-axis) x 8.2 mm  
(Y-axis)

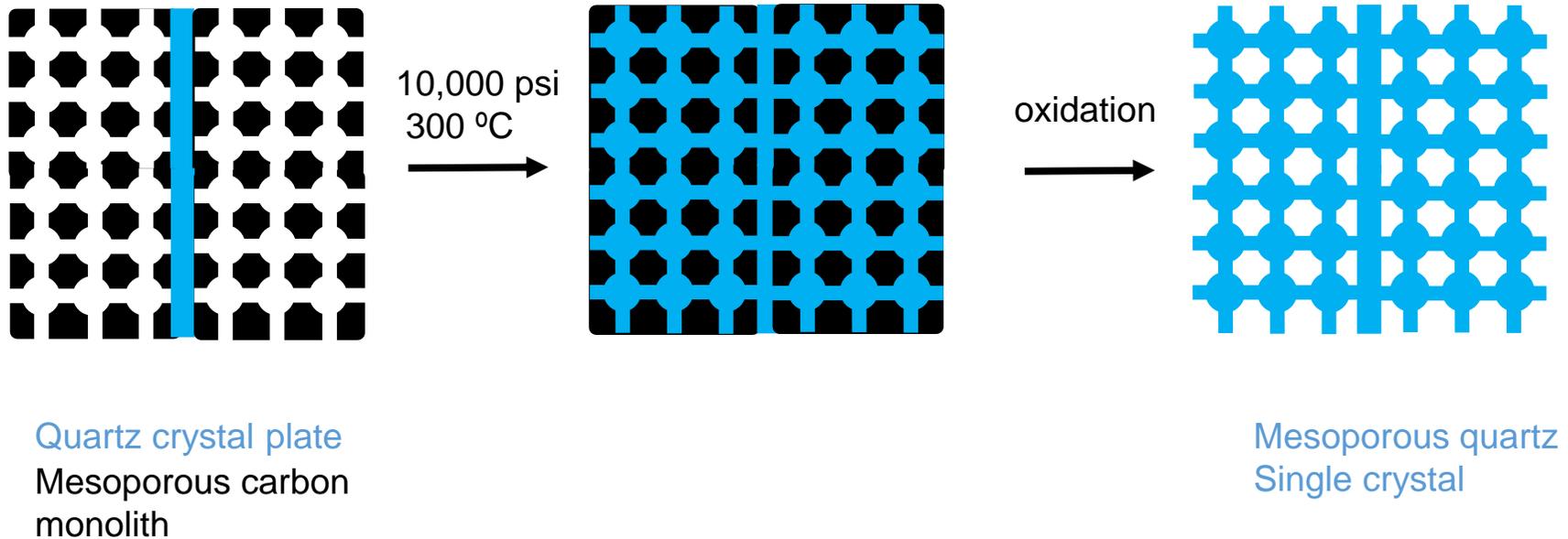
Thickness: 1.2 mm (Z-axis)



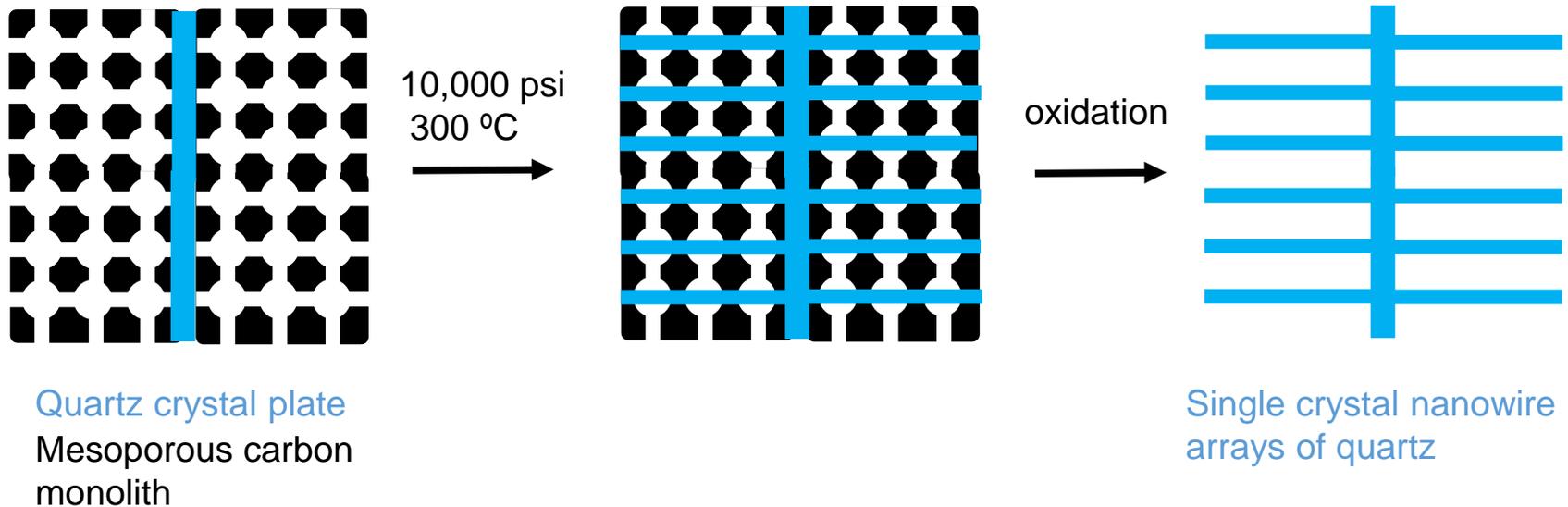
Quartz crystals after growth  
Thickness 7.2 mm (Z-axis)

Ruler is in inches.

# Scalable growth of mesoporous quartz crystals at hydrothermal conditions



# Scalable hydrothermal growth of mesoporous quartz crystals : An alternative scenario



Anisotropic growth rate may lead to quartz nanowires for z-cut seed crystals.  
Different seed crystal cut may be required.

# Scalable hydrothermal growth of mesoporous quartz crystals: Possible extensions

## Growth of mesoporous aluminosilicates?

- Introduction of catalytically active Lewis acid and Brønsted acid sites.
- High stability due to non-zeolitic channel walls.

## Growth of mesoporous titano/iron silicates?

- Introduction of catalytically active Lewis acid sites.
- High stability due to non-zeolitic channel walls.

## Growth of other mesoporous oxide single crystals?

- Band gap tuning of oxidic semiconductors, e.g.  $\text{GeO}_2$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$

# Scalable growth of mesoporous quartz crystals at hydrothermal conditions

Closed knowledge gaps: We will know how to

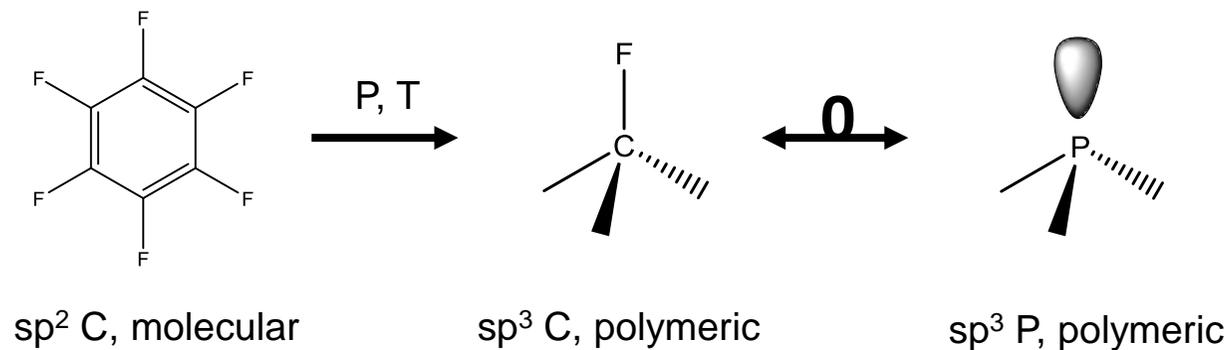
- develop a scalable synthesis method for mesoporous silicas with crystalline walls.
- grow a large single crystals with mesopores in a controlled way.

Energy needs:

- Catalysts and catalyst supports for applications in extreme environments.
- Piezoelectric pressure sensors

# Carbon fluorides

C-F bond: 485 kJ/mol  
C-C bond: 385 kJ/mol  
F-F bond: 155 kJ/mol

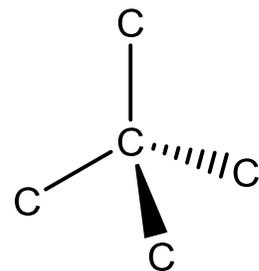


# Carbon fluorides

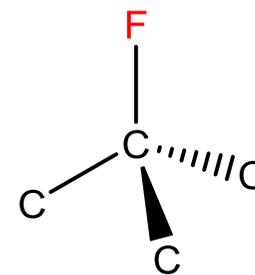
Possible extensions:

$C:F < 1:1$

→ Structures with

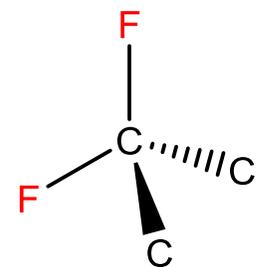


and

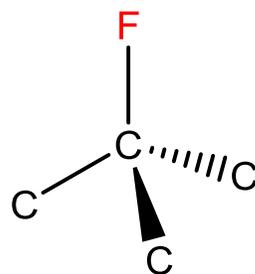


$C:F > 1:1$

→ Structures with

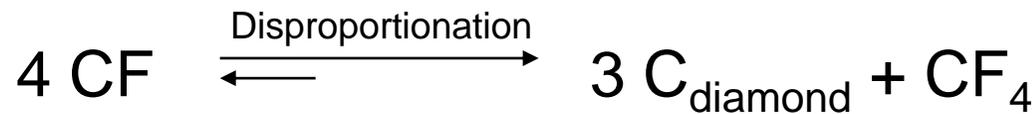
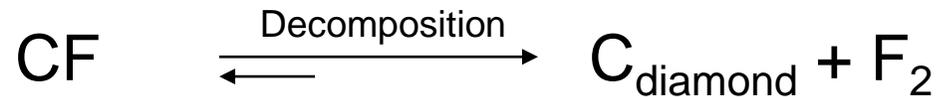


and



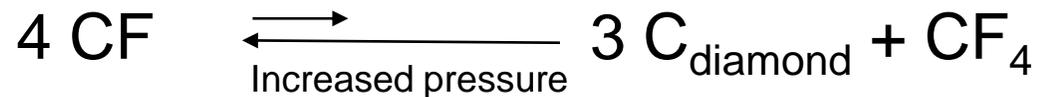
# Carbon fluorides

Possible pitfalls:



Perfluorinated  
diamond (nano)crystals?

Possible solution: LeChatelier's principle



# Carbon fluorides

## Closed knowledge gaps:

- We will know how to produce crystalline  $sp^3$  carbon networks that are fundamentally different from the diamond structure.

## Energy need:

- Need for new ceramic materials.
- High stability due to strong C-C and C-F bonds.
- Quenchable and scalable high pressure phases.
- High hydrophobicity due to F terminated surfaces.