New directions in High-pressure Chemistry with Periodic Mesostructured Materials

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Discovery of Periodic Mesoporous Silicas


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.

- 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

Pressure
Pressure
Pressure
Template removal
Template removal
Template removal
SBA16/Carbon composites at 10 GPa

![Diagram showing X-ray diffraction patterns at various temperatures.]

- (a) RT
- (b) 400 °C
- (c) 800 °C
- (d) 1000 °C
- (e) 1300 °C
- (f) 1400 °C
- (g) 1500 °C
- (h) 1800 °C

Legend:
- ○ Graphite
- ψ Stishovite
- * Coesite
- Δ Diamond
- # Platinum

Intensity (a. u.) vs. 2θ (degree)
Phase diagram of silica
SBA16/C composites at 10 GPa
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 m² g⁻¹
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 ± 9%
Estimated Surface area: 54 m² 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

1. $\text{H}^+ / \text{H}_2\text{O}$
2. $\Delta$

Mesoporous diamond

OEt
EtO
Si

？

Triblock-copolyether

OH

1. $\text{H}^+ / \text{H}_2\text{O}$
2. $\Delta$

Triblock-copolyether
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_{ex} = 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

50 nm crystals

14 GPa, 3h, 1400 °C.

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?
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:

- Al₂O₃ is more inert than silica.
- Al₂O₃ 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

AAO $\rightarrow$ AAO/C$_{\text{graphite}}$ $\rightarrow$ AAO/C$_{\text{diamond}}$ $\rightarrow$ 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: $T_{\text{diss}} = 375 \degree C$; $T_{\text{growth}} = 350 \degree C$, $P = 9,000 \text{ psi}$

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

Quartz crystal plate
Mesoporous carbon monolith

10,000 psi
300 ºC

oxidation

Mesoporous quartz
Single crystal
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.

Quartz crystal plate
Mesoporous carbon monolith

10,000 psi
300 °C

oxidation

Single crystal nanowire arrays of quartz
Scalable hydrothermal growth of mesoporous quartz crystals: Possible extensions

Growth of mesoporous alumosilicates?
• Introduction of catalytically active Lewis acid and Broensted 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. GeO$_2$, ZnO, 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

sp$^2$ C, molecular  sp$^3$ C, polymeric  sp$^3$ P, polymeric
Carbon fluorides

Possible extensions:

\[ \text{C:F} < 1:1 \quad \rightarrow \quad \text{Structures with} \quad \text{and} \]

\[ \text{C:F} > 1:1 \quad \rightarrow \quad \text{Structures with} \quad \text{and} \]
Carbon fluorides

Possible pitfalls:

\[ \text{CF} \xleftrightarrow{\text{Decomposition}} \text{C}_{\text{diamond}} + \text{F}_2 \]

\[ 4 \text{ CF} \xleftrightarrow{\text{Disproportionation}} 3 \text{ C}_{\text{diamond}} + \text{CF}_4 \]

Perfluorinated diamond (nano)crystals?

Possible solution: LeChatelier’s principle

\[ 4 \text{ CF} \xleftrightarrow{\text{Increased pressure}} 3 \text{ C}_{\text{diamond}} + \text{CF}_4 \]

\[ \text{CF} \leftrightarrow \text{C}_{\text{diamond}} + \text{F}_2 \xleftrightarrow{\text{Increased pressure}} \]
Carbon fluorides

Closed knowledge gaps:

• We will know how to produce crystalline sp³ 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.