Biomaterials Alchemy: Changing the Chemistries, but not Shapes, of Biogenic Structures

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Materials Alchemy: Changing the Chemistries, but not Shapes, of Synthetic Structures

Flexible Cu Antenna on Paper

ZrC/W Rocket Nozzle Liners

Racetrack Resonator Optical Sensor

Porous Si on Dense Si

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(images compiled by Mark Hildebrand)
Diatoms: 3-D Micro/Nanoscale $\text{SiO}_2$ Assembly

10$^5$ species
Each species forms a specific, unique 3-D shape: *genetic precision*

Sustained culturing yields many copies (80 cycles = $2^{80} = 10^{24}$): *massively parallel self-assembly*

$\Rightarrow$ Predominantly comprised of $\text{SiO}_2$

(images compiled by Mark Hildebrand)
Biological Assembly and Shape-preserving Inorganic Conversion

(BASIC)

(U.S. Patents No. 7,615,206; No. 7,204,971; No. 7,067,104)
Use microorganisms as **biofactories** to precisely and rapidly replicate enormous numbers \( (2^n) \) of rigid, 3-D self-assembled, nanoparticle structures:

- **BASIC Paradigm for Bio-Enabled Materials**
  - Use shape-preserving chemical conversion methods to alter the composition for desired properties.
Shape-Preserving Chemical Transformation of Biogenic Structures: Bio-Enabled Materials

◆ Gas/solid reactive conversion of inorganic templates

Displacement Reactions with Bio-inorganic and Synthetic Inorganic Preforms:

- Biological Assembly and Shape-preserving Inorganic Conversion (BASIC) process\(^1\)
  - Exchange reactions of porous SiO\(_2\) templates with Mg\((g)\), TiF\(_4\)(\(g\)), ZrCl\(_4\)(\(g\)), ...}
  - \(\Rightarrow\) Positive replicas of MgO/Si, MgO, Si, SiC, C, TiO\(_2\), ZrO\(_2\), ...

◆ Conformal Coating-based Methods

Layer-by-Layer Deposition onto Bio-organic Templates:

- Surface Sol-Gel process + template removal
  - Alkoxide chemisorption on OH-rich templates + pyrolysis
  - \(\Rightarrow\) Negative replicas of Fe\(_2\)O\(_4\), SnO\(_2\), TiO\(_2\), ZrO\(_2\), BaTiO\(_3\), Eu-BaTiO\(_3\), ...
Aulacoseira Diatom Frustules

Regularly-spaced rows of fine pores (few hundred nm in diameter) running along the capsule wall.
Diatom Alchemy

- MgO
- ZrO$_2$
- TiO$_2$
- Eu-BaTiO$_3$
- Au
- Si
- (Zn,Mn)$_2$SiO$_4$
- SiC
- C

Surface area:
- Si: 540 m$^2$/g
- Eu-BaTiO$_3$: 1,370 m$^2$/g
Gas/Solid Reactive Conversion of Biogenic (Diatom) and Synthetic SiO$_2$ into Replicas of MgO, TiO$_2$, ZrO$_2$, Si, SiC, C

For the reaction:

$$2\text{Mg}(g) + \text{SiO}_2(s) \rightarrow 2\text{MgO}(s) + \text{Si}(s)$$

the relative amounts of the solid products are:

- 65.1 vol% MgO, 34.9 vol% Si

A uniform mixture of these solid products should be comprised of co-continuous MgO and co-continuous Si (i.e., interpenetrating networks of both MgO and Si).
MgO/Si Frustule Replica

Transmission electron image

Epoxy

200 nm
Magnesiothermic Reduction of SiO$_2$ -> Si

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- Selective dissolution of the MgO should then yield an interconnected, highly-porous Si replica of the starting SiO$_2$ template:
  
  \[ \text{SiO}_2 \rightarrow 2\text{MgO(s)} + \text{Si(s)} \rightarrow \text{Si(s)} \]
Conversion into Si-based Replicas

Starting Frustules

650°C, 2.5 h, Mg:SiO₂ = 2.5:1

1M HCl, 4 h

(average Si crystal size from Scherrer analysis = 8.1 nm)
Magnesiothermic Reduction of SiO$_2$ -> Si

- For the reaction:
  
  \[2\text{Mg}(g) + \text{SiO}_2(s) \Rightarrow 2\text{MgO}(s) + \text{Si}(s)\]

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- Selective dissolution of the MgO should then yield an interconnected, highly-porous Si replica of the starting SiO$_2$ template:
  
  \[\text{SiO}_2 \Rightarrow 2\text{MgO}(s) + \text{Si}(s) \Rightarrow \text{Si}(s)\]

  \[\Delta V_m/V_m (\text{SiO}_2 \rightarrow \text{Si}) = -55.8 \text{ to } -58.5\%\]
Conversion into Si Replicas

Secondary electron image

Surface Area: 541.0 m²/g (BET analysis)

Si nanoparticle replica (after etching in 1 M HCl for 4 h)

Porous Si for Lithium Ion Battery Anodes

(Reaction of <2.5 μm SiO(s) powder with Mg(g) at a peak temperature of 500°C for 12 h, then MgO dissolution)

Transmission Electron Image

(Reaction of <2.5 µm SiO(s) powder with Mg(g) at a peak temperature of 500°C for 12 h, then MgO dissolution)

Applications for Mg-derived Porous Si Replicas

**Porous silicon anodes for lithium ion batteries**


Applications for Mg-derived Porous Si Replicas

- **High-sensitivity sensors**

- **Thermoelectric particles**

- **Photoluminescent Particles**

- **Inverse Opals**

- **Drug Delivery**

- **Photocathode**

- **Electromagnetic Wave Absorption**
Reactive Conversion into SiC and C Replicas

\[
\text{SiO}_2 + \text{Mg}(g) \rightarrow 2\text{MgO} + \text{Si} \rightarrow \text{Si}
\]

\[
\text{Si} + \text{CH}_4(g) \rightarrow \text{SiC} + 2\text{H}_2(g) \\
\text{(1200}^\circ\text{C, 12 h)}
\]

\[
\text{SiC} + 2\text{Cl}_2(g) \rightarrow \text{C} + \text{SiCl}_4(g) \\
\text{(950}^\circ\text{C, 2 h)}
\]

Sandhage Group
Reactive Conversion into Porous C Replicas

Secondary electron image

BET Surface Area: 1,370 m²/g!

EDX analysis
Pt Nanoparticles within C Frustule Replicas

HRTEM image
(Pt deposition from Pt(CO)$_2$Cl$_2$ vapor)
At the anode of a proton exchange membrane (PEM) fuel cell, $\text{H}_2(\text{g})$ is oxidized to yield protons and electrons:

$$\text{H}_2(\text{g}) \Rightarrow 2\text{H}^+ + 2\text{e}^-$$

At the cathode, $\text{O}_2(\text{g})$ undergoes the following reduction reaction:

$$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$$

The oxygen reduction reaction is relatively sluggish and significant R&D on catalysts and catalyst supports is underway.
Catalysis of the Oxygen Reduction Reaction

Current Density (mA cm^{-2})

Time (sec)

at 0.8V (vs. NHE)

Pt/C_F
Pt/C_S
Pt/C_V

(RDE, 2000 rpm, 0.5 M H_2SO_4 solution)

(with Prof. Meilin Liu, School of MSE, Georgia Tech)
### Surface Area, Pore Volume Analyses

<table>
<thead>
<tr>
<th>Specimen</th>
<th>SSA (m²g⁻¹)</th>
<th>SMiV (cm³g⁻¹)</th>
<th>SMeV (cm³g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_F$</td>
<td>1370</td>
<td>0.282</td>
<td>1.53</td>
</tr>
<tr>
<td>$C_V$</td>
<td>227</td>
<td>0.0232</td>
<td>0.413</td>
</tr>
<tr>
<td>$C_S$</td>
<td>1230</td>
<td>0.286</td>
<td>1.40</td>
</tr>
</tbody>
</table>

$C_F = C$ frustule replicas (10-11 µm dia.); $C_V = C$ black (Vulcan XC-72R, 4.9 µm ave. dia.); $C_S = C$ replicas of SiC powder (8.7 µm ave. dia.).

SSA = specific surface area; SMiV = specific micropore (<2 nm dia.) volume; SMeV = specific mesopore (2-50 nm dia.) volume.
Hollow frustule replicas => short diffusion distance for oxygen! (half wall thickness ~ 700 nm)