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

Porous Si on Dense Si

Racetrack Resonator Optical Sensor

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Pollen Grains

- Utilized by plants for the transfer of male genetic material, and is widely available in large quantities
- Adapted for wind-based (anemophilous plants) or insect-based (entomophilous plants) pollination
- A wide variety of species-specific shapes and surface morphologies exist among pollen grains
- Pollen adhesion is achieved via:
  - entanglement (with insect hair)
  - van der Waals attraction
  - capillarity/wetting of pollenkitt
- The pollen exine (outer layer) consists of sporopollenin, a robust polymer rich in carboxylic acids

Sunflower (*Helianthus annuus*) Pollen

Secondary electron images
Surface Sol-Gel Processing

Chemisorption of Metal Alkoxide

Water Hydrolysis

(obtained from S. Fujikawa, R. Takaki, T. Kunitake, Langmuir, 21, 8899 (2005))
Surface Sol-Gel Processing

Resorption of Metal Alkoxide

Layering of Ultrathin Metal Oxide

**Conformal Fe-O Coating of Sunflower Pollen**

Native Sunflower Pollen  
Fe-O Coated Pollen

Secondary electron images  
(30 SSG cycles with Fe(III) isopropoxide)

Organic Pyrolysis

Thermogravimetric Analyses

(5°C/min to 600°C in air)

Iron Oxide Sunflower Pollen Replicas

Fe-O Coated Pollen

Fe$_3$O$_4$ Pollen Replica

Secondary electron images

(30 SSG cycles with Fe(III) isopropoxide; 600°C, 4 h, air; Rhines pack, 550°C, 2 h)

Adhesion Testing of Pollen and Pollen Replicas

Multi-modal Adhesion of Fe$_3$O$_4$ Replicas

![Graph showing force versus vertical distance for different conditions: Si, Mag Center, Mag Edge.](image)

- Force (nN)
- Vertical Distance (µm)
- Sandhage Group

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Tailorable Long Range Magnetic Adhesion

Papilio blumei Butterfly

2 cm
Green Ventral Scale of P. blumei Butterfly
Green Ventral Scale of P. blumei Butterfly

Secondary electron image

Concavity

Ridge

2 µm
Eu-doped BaTiO₃ Replicas of P. blumei Scales
Eu-doped BaTiO$_3$ Replicas of P. blumei Scales

Secondary electron images

BaTiO$_3$

Eu-BaTiO$_3$

488 nm excitation, >585 nm emission
Labeling with Eu-BaTiO$_3$ P. blumei Replicas

(Eu-BaTiO$_3$ replica scales on cellulose filter paper)
Labeling with Eu-BaTiO₃ P. blumei Replicas

(Eu-BaTiO₃ replica scales on cellulose filter paper)
Fe$_3$O$_4$-coated Frustules

Secondary electron images

(21 SSG cycles involving Fe(III) isopropoxide, 550°C/2 h in Fe/Fe$_3$O$_4$ Rhines pack)
As Adsorption Experiments

<table>
<thead>
<tr>
<th>Test Material</th>
<th>SSA (m²/g)</th>
<th>Porosity (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Fe₃O₄ (CM)</td>
<td>44.0</td>
<td>68</td>
</tr>
<tr>
<td>Fe₃O₄ Diatoms (MD)</td>
<td>4.7</td>
<td>55</td>
</tr>
</tbody>
</table>

peristaltic pump

Asₐq solution

filter assembly

test material

filter paper

SS mesh
As Removal from Water w/Fe$_3$O$_4$-coated Frustules

As(V)

Time (h)

SSA   Porosity
(m$^2$/g)  (vol%)

CM: 44.0  68
MD: 4.7   55

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As Removal from Water w/Fe$_3$O$_4$-coated Frustules

As(III)

\[ q \text{ (mg/kg)} \]

Time (h)

\[ \text{SSA (m}^2/\text{g)} \quad \text{Porosity (vol\%)} \]

CM: 44.0 68
MD: 4.7 55
Patented shape-preserving gas/solid displacement reactions have been used to convert microscale, nanostructured 3-D bioinorganic and synthetic inorganic structures (silica diatom frustules, synthetic silicas) into replicas of other functional materials (e.g., highly porous Si, SiC, C, C/Pt).

Layer-by-layer conformal coating and thermal treatment processes have been used to convert microscale, nanostructured 3-D bio-organic structures (pollen grains, butterfly scales) and bio-inorganic structures (diatom frustules) into replicas comprised of a variety of functional oxides (e.g., Fe$_3$O$_4$, SnO$_2$, TiO$_2$, ZrO$_2$, BaTiO$_3$, Eu-BaTiO$_3$).
Shape-Preserving Chemical Transformation of Biogenic Structures: Bio-Enabled Materials

- High surface area electrodes
  - Anodes for batteries (Si diatom frustule replicas)
  - Cathodes for fuel cells (Pt/C diatom frustule replicas)

- Rapid, sensitive, microscopic sensors
  - Alcohol-sensing (TiO$_2$ diatom frustule replicas)

- Tailored adhesive microparticles
  - Shaped magnetic particles (Fe$_3$O$_4$ pollen replicas)

- Optical micromarkers
  - Shaped photoluminescent particles (Eu-BaTiO$_3$ butterfly scales)

- Water (and other fluid) purification
  - Arsenic adsorption (Fe$_3$O$_4$-coated diatom frustule replicas)
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- U.S. AFOSR/AFRL: BIONIC Center of Excellence
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- U.S. Dept. of Defense MURI program
  - BIO-OPTICS (Bio-Inspired Optics: Offering Physical and Technological Insights into Color and Structure)
  - BIO-PAINTS (Bio-enabled Particle Adherents for Interrogative Spectroscopy)
- U.S. Dept. of Energy, Office of Basic Energy Sciences
  (Biomolecular Materials program)
- DARPA (CIPhER program)

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Biomaterials Alchemy: Questions? Suggestions?

The Alchymist, Joseph Wright, 1771