Conformal Coating of/by Sustainable Materials for New Functionalities

Diatom-derived Porous C Replica

Diatom-derived Au Replica

Eu-BaTiO$_3$
P. blumei Replica

Fe$_3$O$_4$ Sunflower Pollen Replica

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Chemical Tailoring of/with Renewable Materials

- Chemical functionalization of renewable biotemplates with synthetic materials
  - Bio-inorganic structures: diatom microshells
  - Bio-organic structures: micro/nanocellulose, pollen

- Chemical functionalization of synthetic templates with the aid of renewable biomolecules
  - Protein-enabled porous oxide coatings
  - Protein-enabled hybrid oxide/organic coatings
Diatoms: 3-D Micro/Nanoscale $\text{SiO}_2$ Assembly

$10^4$-$10^5$ 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)
Aulacoseira Diatom Frustules (DE)

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

Secondary electron images
MgO Replicas

Energy-dispersive x-ray analysis

Diatom Alchemy

MgO

ZrO$_2$

TiO$_2$

Eu-BaTiO$_3$

Au

Si

(Zn,Mn)$_2$SiO$_4$

Epoxy

C

$4 \mu m$

$4 \mu m$

$4 \mu m$

$4 \mu m$

$4 \mu m$

$4 \mu m$

$540 \text{ m}^2/\text{g}$

$1,370 \text{ m}^2/\text{g}$
Coating of Diatom Frustules and CNCs with Metals (Au, Cu, Ag, Ni) via Highly-Conformal Electroless Deposition
Surface Functionalization of Frustules

Diatom frustule with a modest concentration of -OH groups
**Surface Functionalization of Frustules**

Diatom frustule with a modest concentration of -OH groups

(with Marder group, Georgia Tech)

\[(\text{EtO})_3\text{Si} - \text{NH}_2\]

(3-aminopropyl)triethoxysilane in NH\(_4\)OH (aq.), reflux
Aminosilanized diatom frustule with a modest concentration of -NH\textsubscript{2} groups
Surface Functionalization of Frustules

Aminosilanized diatom frustule with a modest concentration of -NH₂ groups

Step A

dipentaerythritol penta-/hexaacrylate in EtOH;
R: COCH=CH₂ or H
Surface Functionalization of Frustules

Diatom frustule with polyacrylate groups

Step B

tris(2-aminoethyl) amine in EtOH
Surface Functionalization of Frustules

Diatom frustule with polyamine groups

Repeat steps A and B
Copper “Replica” of an Aulacoseira Frustule

Secondary electron image

(Aminosilanization; amine amplification; PdCl$_2$ sensitization; Cu deposition, SiO$_2$ dissolution)
Copper “Replica” of an Aulacoseira Frustule

Secondary electron image

EDX analyses
Coscinodiscus asteromphalus Diatom Frustules

Secondary electron images

(with Perry group, School of Chemistry & Biochemistry, Georgia Tech)
Au Replica of an *C. asteromphalus* Frustule

Secondary electron images

(Aminosilanization; *amine amplification*; HAuCl$_4$/NaBH$_4$ sensitization; electroless Au deposition; SiO$_2$ dissolution)
Au Replica of an *C. asteromphalus* Frustule

Secondary electron images

(Aminosilanization; *amine amplification*; HAuCl$_4$/NaBH$_4$ sensitization; electroless Au deposition; SiO$_2$ dissolution)
Au Replica of an *C. asteromphalus* Frustule

**Secondary electron images**

(Aminosilanization; *amine amplification*; HAuCl$_4$/NaBH$_4$ sensitization; electroless Au deposition; SiO$_2$ dissolution)
Secondary electron images of an ion-milled cross-section
(Aminosilanization; amine amplification; HAuCl$_4$/NaBH$_4$
sensitization; electroless Au deposition; selective SiO$_2$ dissolution)
Extraordinary Optical Transmission


\[ \lambda \propto a_o \left\{ \varepsilon_m \varepsilon_d / [\varepsilon_m + \varepsilon_d] \right\}^{1/2} \]
Extraordinary IR Transmission through a Au Replica of a C. asteromphalus Frustule

Optical reflection image

Experimental IR transmission
Ink jet-printed catalyst, then electroless Cu deposition onto paper

2.4 GHz meander monopole flexible antenna (with M. Tentzeris, et al.)
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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.

The Surface Sol-Gel Process

Chemisorption of Metal Alkoxide

Water Hydrolysis
The Surface Sol-Gel Process

Resorption of Metal Alkoxide

Layering of Ultrathin Metal Oxide
Automated Surface Sol-Gel System
Automated Surface Sol-Gel System

Pumps

Vacuum Filtration Unit

Alkoxide

Waste

Computer

Georgia Institute of Technology
Automated Surface Sol-Gel System
Automated Surface Sol-Gel System

Pumps

Water
Solvent
Alkoxide

Vacuum Filtration Unit

Waste

Computer

Georgia Institute of Technology
Automated Surface Sol-Gel System

Pumps

Vacuum Filtration Unit

Vacuum Drying

Waste

Water
Solvent
Alkoxide

Computer

Georgia Institute of Technology
Sunflower (Helianthus annuus) Pollen

Secondary electron images

(with Meredith group, School of Chemical & Biomolecular Engineering, Georgia Tech)
Conformal Fe-O Coating of Sunflower Pollen

Native Sunflower Pollen  Fe-O Coated Pollen

Secondary electron images

(30 SSG cycles with Fe(III) isopropoxide)
Fe$_2$O$_3$ Sunflower Pollen Replicas

Fe-O Coated Pollen

Fe$_2$O$_3$ Pollen Replica

Secondary electron images

(30 SSG cycles with Fe(III) isopropoxide; 600°C, 4 h, air)
Fe₃O₄ Sunflower Pollen Replicas

Fe₂O₃ Pollen Replica

Fe₃O₄ Pollen Replica

Secondary electron images

(30 SSG cycles with Fe(III) isopropoxide; 600°C, 4 h, air; Rhines pack, 550°C, 2 h)
Fe₃O₄ Sunflower Pollen Replicas

X-ray Diffraction Analysis

(Scherrer analysis: 34 nm average crystal size)

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

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

ARRRRSSSRPIRRRRPRRRTTRRRRAGRRRR

- Short protein (31 amino acids)
- Highly basic (pI = 13.5) with 64.5% arginine residues
- Commercially available in large quantities (harvested from salmon, herring, rainbow trout, tuna, sturgeon, dogfish)
Protamine-Enabled Layer-by-Layer TiO$_2$ Deposition

**STEP 1:**
- a) adsorb protein
- b) remove unbound protein by washing

**STEP 2:**
- a) add aqueous solution of titania precursor (TiBALDH)
- b) remove excess TiBALDH by washing

**STEP 3:**
- a) adsorb protein
- b) remove unbound protein by washing
Porous Wall TiO$_2$ Nanotube Arrays via Protamine-Enabled LbL Deposition

- Synthesize a porous anodic alumina membrane (PAAM)
- Deposit a protamine/Ti-O coating of controlled thickness onto the PAAM template
- Heat treatment to pyrolyze the protamine and crystallize the TiO$_2$ to yield a porous anatase TiO$_2$ coating
Porous Wall TiO₂ Nanotube Arrays via Protamine-Enabled LbL Deposition

- Synthesize a porous anodic alumina membrane (PAAM)
- Deposit a protamine/Ti-O coating of controlled thickness onto the PAAM template
- Heat treatment to pyrolyze the protamine and crystallize the TiO₂ to yield a porous anatase TiO₂ coating
- Selective alumina dissolution to yield a freestanding, porous wall TiO₂ nanotube array
Porous Anodic Alumina Template

Top-down view

Secondary electron image

(Al anodized in 14 wt% H$_3$PO$_4$, 6 mA/cm$^2$, 4°C; Al backing dissolved in 0.25 M CuCl$_2$/6 M HCl; Al$_2$O$_3$ base dissolved in 3 M NaOH)

Porous Anodic Alumina Template

Cross-sectional view (fractured surface)

Secondary electron image

(AI anodized in 14 wt% H₃PO₄, 6 mA/cm², 4°C; Al backing dissolved in 0.25 M CuCl₂/6 M HCl; Al₂O₃ base dissolved in 3 M NaOH)

Titania/Protamine-coated PAAM Template

Top down view (after 8 protamine/TiBALDH deposition cycles)
Titania/Protamine-coated PAAM Template

Secondary electron image

(after 8 protamine/TiBALDH deposition cycles)
Aligned, Porous-Wall, TiO$_2$ Nanotube Arrays

(8 deposition cycles; heating at 5$^\circ$C/min to 650$^\circ$C, hold for 3 h in air; selective PAAM dissolution in NaOH; bonding to TiO$_2$-coated FTO/glass substrate at 500$^\circ$C for 1 h)
Enhanced Molecular Loading of Porous-wall TiO$_2$ Nanotubes

Ave. N719 dye loading of sol-gel-derived TiO$_2$ nanotube arrays (Kang, et al.):

$$7.42 \times 10^{-5} \text{ mol/g TiO}_2$$

Ave. N719 dye loading of protamine-derived TiO$_2$ nanotube arrays:

$$1.63 \times 10^{-4} \text{ mol/g TiO}_2$$
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Protamine-induced TiO$_2$ Coating on Diatom SiO$_2$

Secondary electron image

EDX Pattern

(12 protamine/TiBALDH cycles; drying)
Protamine-induced TiO$_2$ Coating on Diatom SiO$_2$

Secondary electron image

XPS Pattern

(12 protamine/TiBALDH cycles; drying)
Thermogravimetric Analysis of Coating

Percentage of Starting Weight

(5°C/min to 650°C in air)

13% => Appreciable entrapment of protamine in the oxide coating!
Glucose oxidase, GOx, is an oxidoreductase enzyme that can accept electrons from glucose to form \( \text{H}_2\text{O}_2 \) (an anti-microbial agent):

- GOx has been cross-linked with protamine (PA) to yield a hybrid (GOx-PA) molecule.
Layer-by-Layer GOx-PA/Oxide Deposition

Layer 2
Enhanced Stability of GOx-PA within SiO$_2$ or TiO$_2$

- The thermal stability of GOx activity (at 65°C) is significantly enhanced within SiO$_2$ or TiO$_2$ coatings (A):

- Stability against proteolysis (24 h exposure to pronase) is also significantly enhanced (B).
Attractive Characteristics of Protein-Enabled Coatings

- Functional coatings can be formed under gentle, low-energy conditions (ambient temperature and pressure, neutral or near neutral pH)
- Biomolecules used to generate functional coatings can be sustainable (i.e., biologically regenerated)
- Such gentle processing allows for functional hybrid (e.g., enzyme/oxide) coatings
- Layer-by-layer, conformal deposition of coatings can be achieved on 3-D templates (not line of sight)
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Functional Sustainable Coatings/Materials

◆ **(Bio)Chemical properties**
  - Hydrophilic vs. hydrophobic surfaces
  - Adsorptive
  - Catalytic
  - Anti-microbial

◆ **Mechanical properties**
  - Physical barrier to fluids
  - Local (scratch) and overall wear resistance

◆ **Optical properties**
  - Color and/or visible transparency
  - Ultraviolet or infrared absorption

◆ **Other properties**
  - Electronic
  - Magnetic
Potential Applications

- Chemical syntheses (via rapid, flow-through catalysis)
- Water purification (via rapid filtration, adsorption)
- Enhanced cleanup of spills
- Odor control
- Packaging of food, medicine (antimicrobial, UV absorption, barrier to water)
- Skin care (e.g., UV protection)
- Static control (electrically-conductive coatings)
- Tailored color (adjustment of refractive index; use of inorganic pigments or fluorescent agents)
- Fillers of controlled shape/size (for enhanced stiffness, wear resistance, etc.)
- Active coatings (e.g., for sensing)
Some Take Home Messages from this Presentation (Ken H. Sandhage)

- Possible applications of the insights and techniques from this presentation
  - Sustainable biotemplates can be conformally coated with a variety of functional materials (ceramics, metals, hybrids) by scalable wet-chemical methods
  - Such coatings enable a host of new properties (catalytic, antimicrobial, optical, electronic, magnetic)

- Barriers and challenges to success
  - Identification of products/markets (low-hanging fruit)
  - Scaleup of tailored process/products

- Additional research opportunities
  - Fundamental understanding of the rate-limiting kinetic mechanisms controlling the surface reactions via in-situ analyses
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