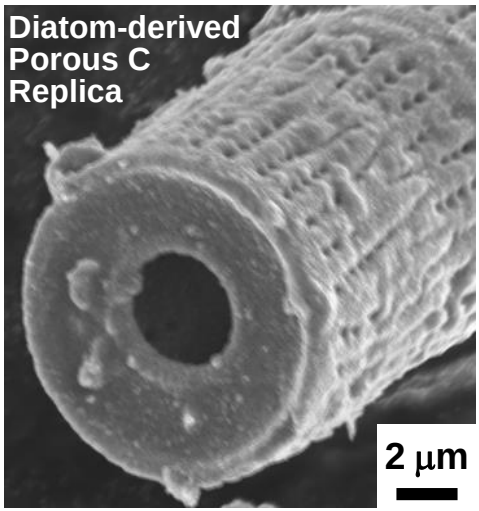
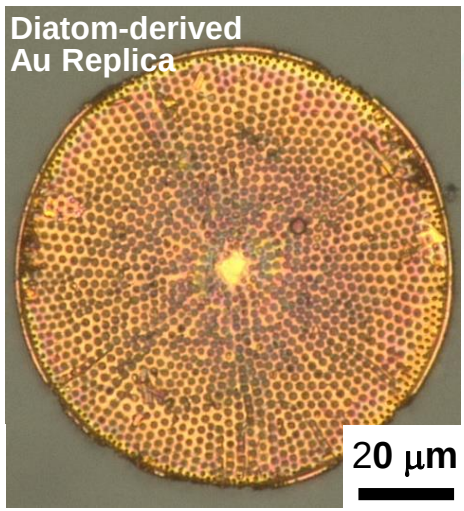
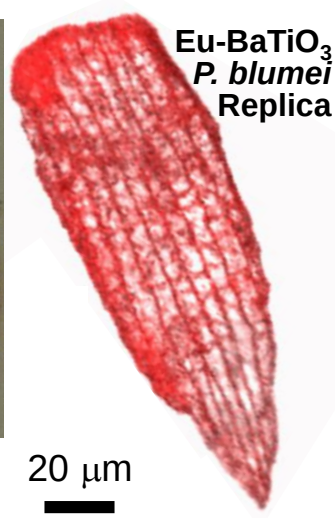
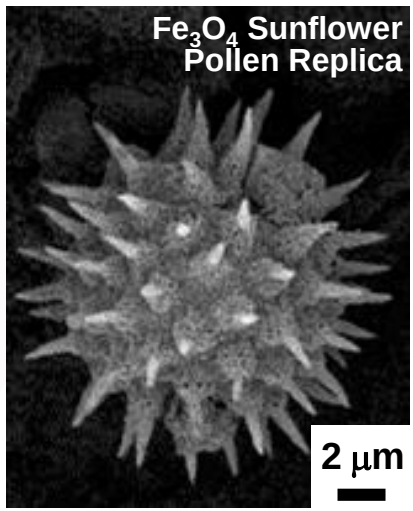
Biomaterials Alchemy: Changing the Chemistries, but not Shapes, of Biogenic Structures









Ken H. Sandhage

Reilly Professor of Materials Engineering
School of Materials Engineering
Purdue University
West Lafayette, IN

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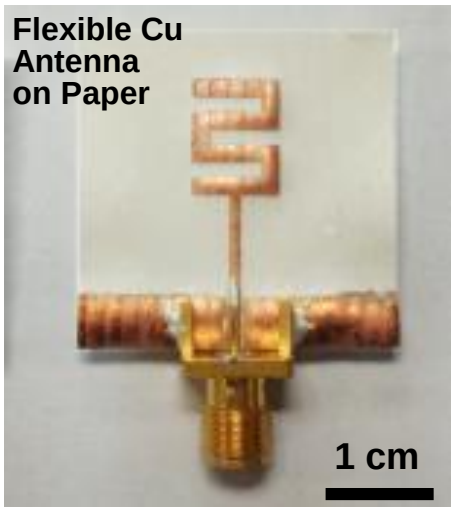
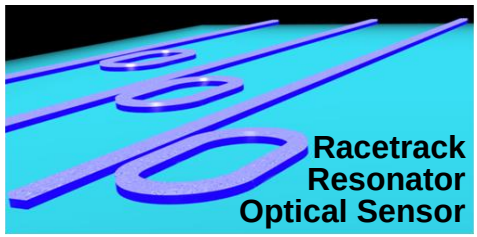
Materials Alchemy: Changing the Chemistries, but not Shapes, of Synthetic Structures





Ken H. Sandhage

Reilly Professor of Materials Engineering
School of Materials Engineering
Purdue University
E-mail: sandhage@purdue.edu

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Research Colleagues

Graduate Students:

Zhihao Bao[1,2]
Dan Berrigan[1,3]
Philip Brooke[1]
Vincent Chen[1]
Stan Davis[1]
Matt Dickerson[1,3]
Brandon Goodwin[1]
Ismael Gomez[1]
Ari Gordin[1]
SungHwan Hwang[4]
Jiaqi Li[4]
Dan Sabo[1]
Taylor Shapiro[1,5]
Sam Shian[6]
Jonathan Vernon[1,3]
Michael Weatherspoon[1,6]

Post-Docs/Research Scientists

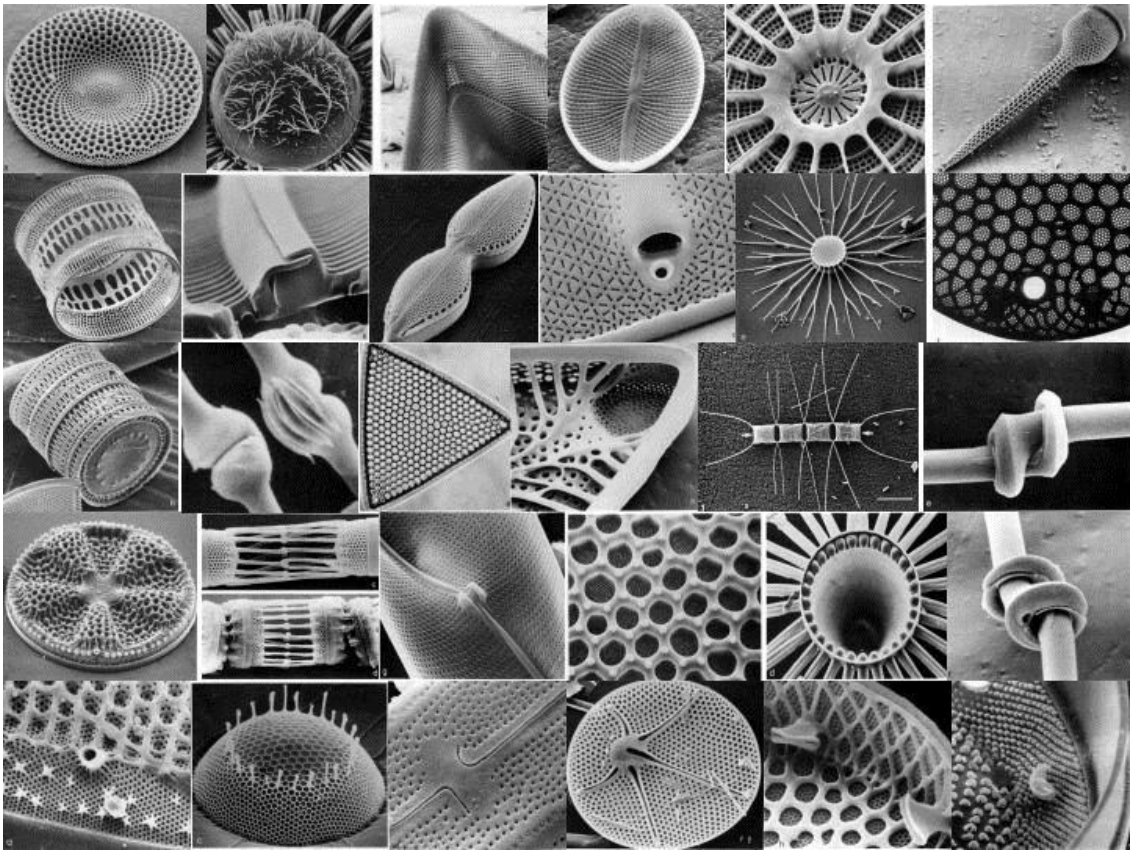
Ye Cai[1]
Vincent Chen[1]
Yunnan Fang[1]
Michael Haluska[1]
Guojie Wang[1]
Yunshu Zhang[1]

Collaborating Research Groups:

Ali Adibi[1]
Michael Durstock[3]
Mark Hildebrand[8]
Nils Kröger[1,9]
Meilin Liu[1]
Seth Marder[1]
Carson Meredith[1]
Rajesh Naik[3]
Joe Perry[1]
Robert Snyder[1]
Mohan Srinivasarao[1]
John Zhang[1]

[1]Georgia Institute of Technology; [2]Tongji University; [3]Air Force Research Laboratory/Wright Patterson Air Force Base; [4]Purdue University; [5]Georgia Perimeter College; [6]Harris Corporation; [7]Scripps Institution of Oceanography; [8]TU Dresden

Diatoms: 3-D Micro/Nanoscale SiO_2 Assembly

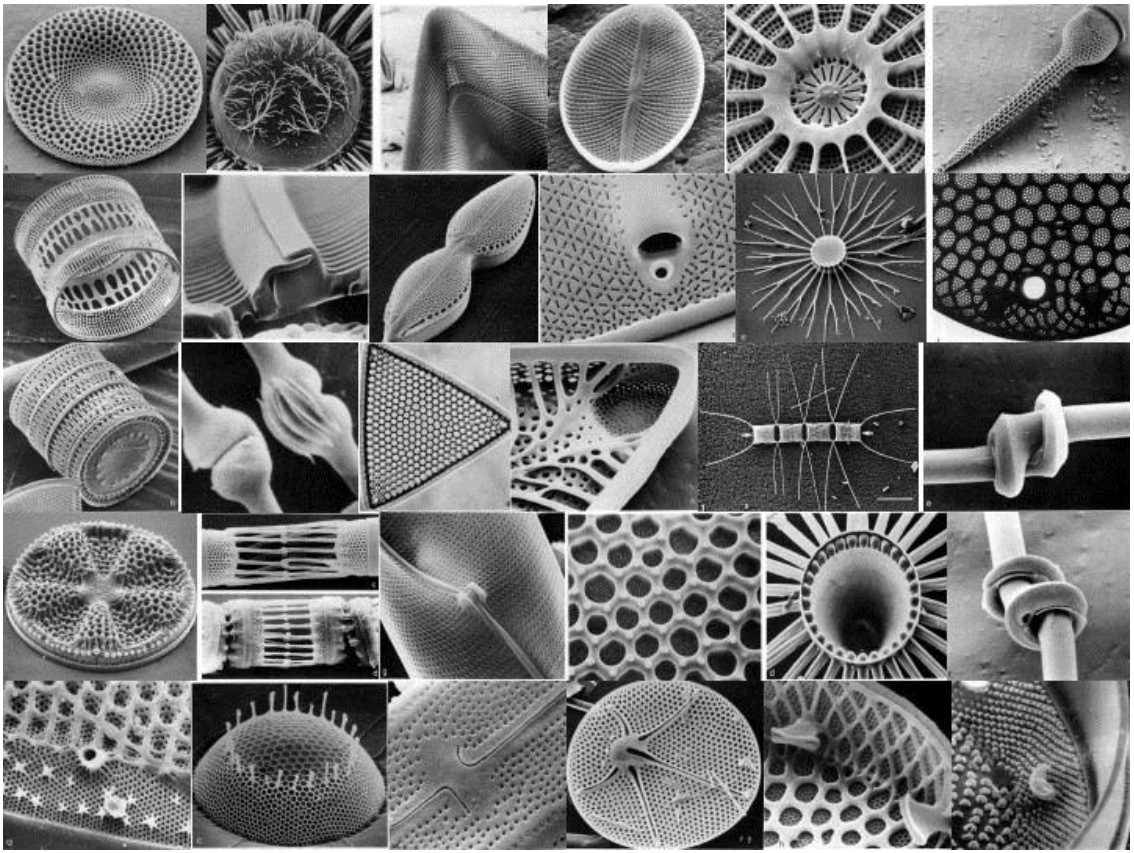


Nature's Nanotechnologists!

F. E. Round, R. M. Crawford, D. G. Mann, The Diatoms: Biology and Morphology of the Genera, Cambridge University Press, 1990

(images compiled by Mark Hildebrand)

Diatoms: 3-D Micro/Nanoscale 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*

⇒ Predominantly comprised of SiO_2

F. E. Round, R. M. Crawford, D. G. Mann, The Diatoms: Biology and Morphology of the Genera, Cambridge University Press, 1990

(images compiled by Mark Hildebrand)

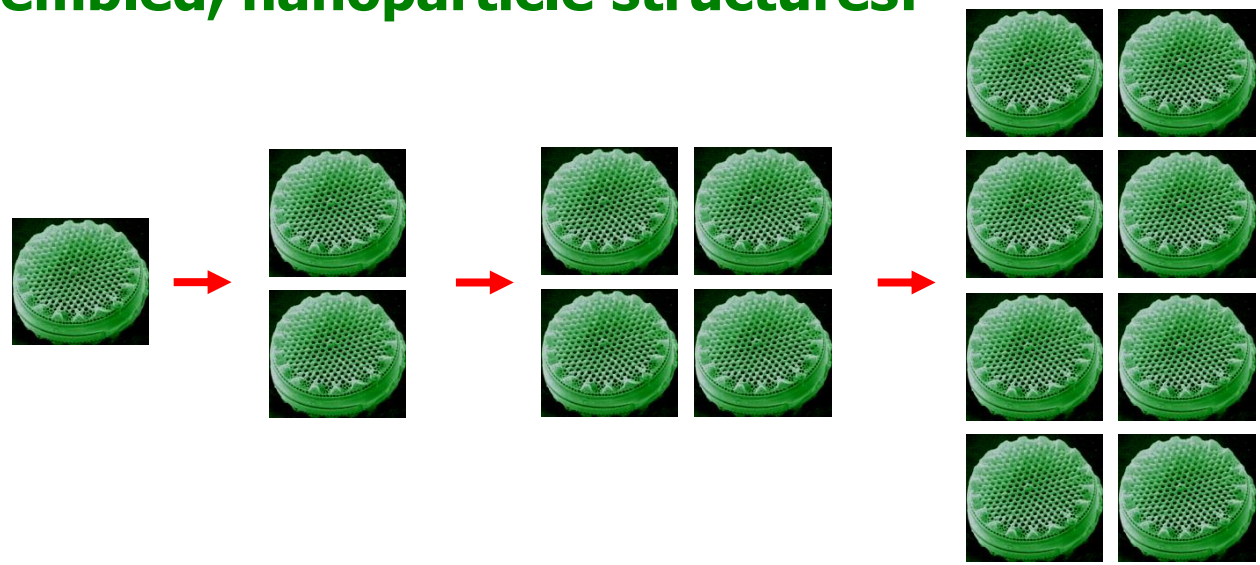
Biological Assembly and Shape-preserving Inorganic Conversion

(BASIC)

(U.S. Patents No. 7,615,206; No. 7,204,971; No. 7,067,104)

BASIC Paradigm for Bio-Enabled Materials

- Use microorganisms as <u>biofactories</u> to precisely and rapidly replicate enormous numbers (2^n) of rigid, 3-D self-assembled, nanoparticle structures:



- Use shape-preserving chemical conversion methods to alter the composition for desired properties.

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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), ...}

    -> 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}

    -> Negative replicas of Fe_3O_4, SnO_2, TiO_2, ZrO_2, $BaTiO_3$, Eu-$BaTiO_3$, ...

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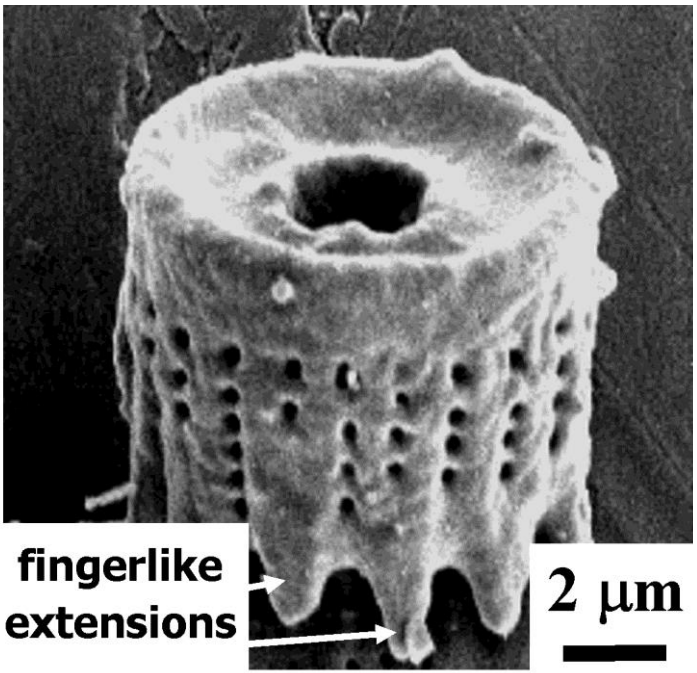
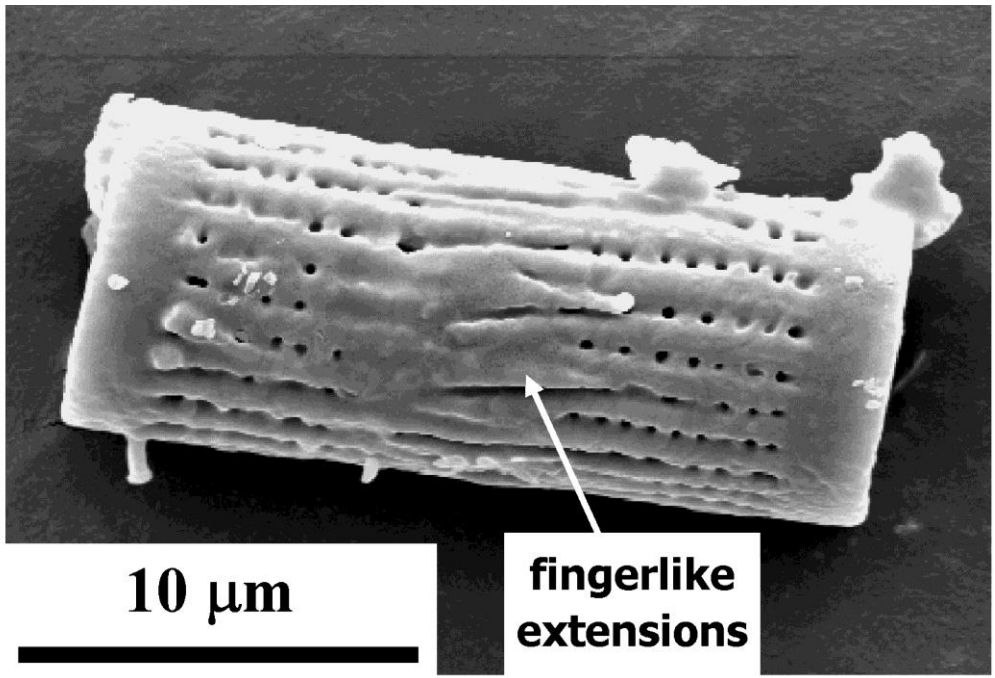
Aulacoseira Diatom Frustules





Secondary electron images

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

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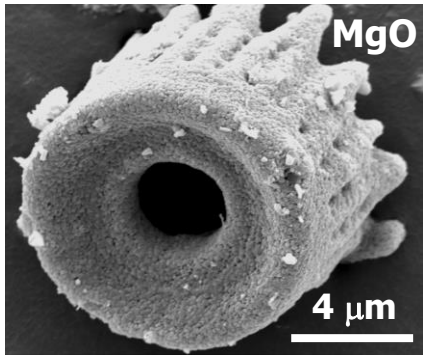
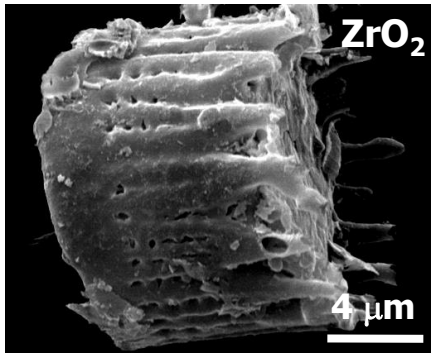
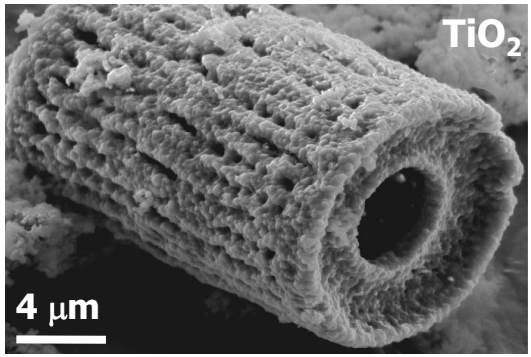
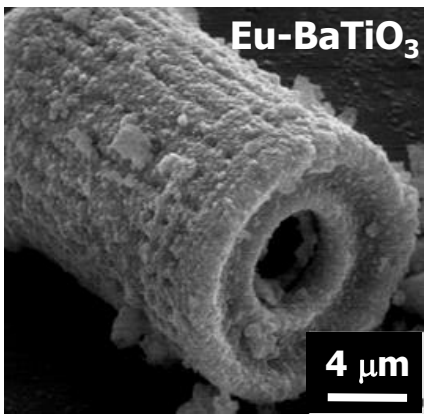
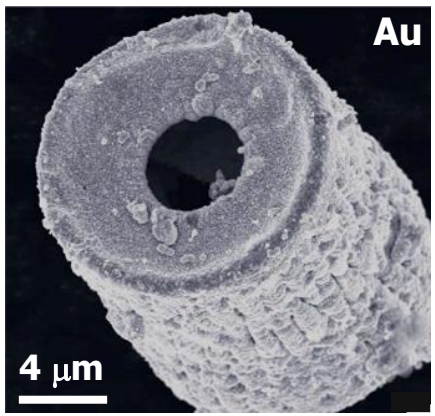
Diatom Alchemy

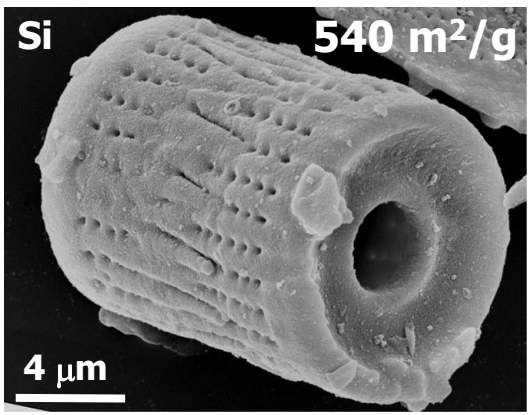


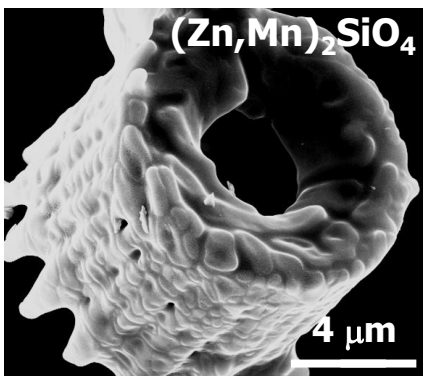


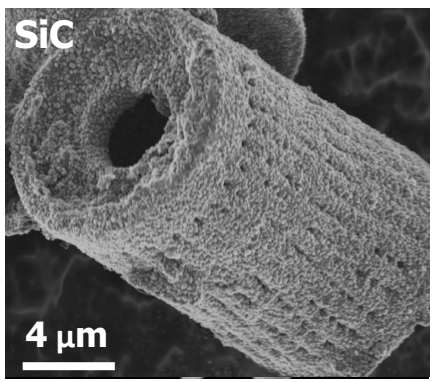


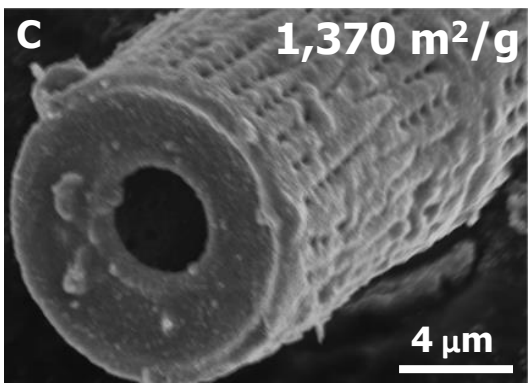












Gas/Solid Reactive Conversion of Biogenic (Diatom) and Synthetic SiO_2 into Replicas of MgO, TiO_2, ZrO_2, Si, SiC, C

- K. H. Sandhage, et al., *Adv. Mater.*, 14, 429 (2002)
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- Y. Cai, et al., *J. Am. Ceram. Soc.*, 88, 2005 (2005)
- M. S. Haluska, et al., *Rev. Sci. Instr.*, 76, 126101 (2005)
- K. H. Sandhage, et al., *Int. J. Appl. Ceram. Technol.*, 2, 317 (2005)
- S. Shian, et al., *J. Am. Ceram. Soc.*, 89, 694 (2006)
- S.-J.Lee, et al., *J. Am. Ceram. Soc.*, 90, 1632 (2007)
- E. M. Ernst, et al., *J. Mater. Res.*, 22, 1121 (2007)
- Z. Bao, et al., *Nature*, 446, 172 (2007)
- R. F. Shepherd, et al., *Adv. Mater.*, 20, 4734 (2008)
- S. Shian, et al., *Rev. Sci. Instr.*, 80, 115108 (2009)
- K. H. Sandhage, *JOM*, 62, 32 (2010)
- B. Hatton, et al., *Proc. Nat. Acad. Sci.*, 107, 10354 (2010)
- Z. Bao, et al., *Energy Environ. Sci.*, 4, 3980 (2011)
- K. Chen, et al., *J. Mater. Chem.*, 22, 16196 (2012)
- A. Xing, et al. *Chem. Commun.*, 49, 6743 (2013)
- S. C. Davis, et al., *Adv. Funct. Mater.*, 4611 (2013)
- Z. Xia, et al., *Adv. Opt. Mater.*, 2, 235 (2014)

Magnesiothermic Reduction of SiO_2 -> Si

- **For the reaction:**

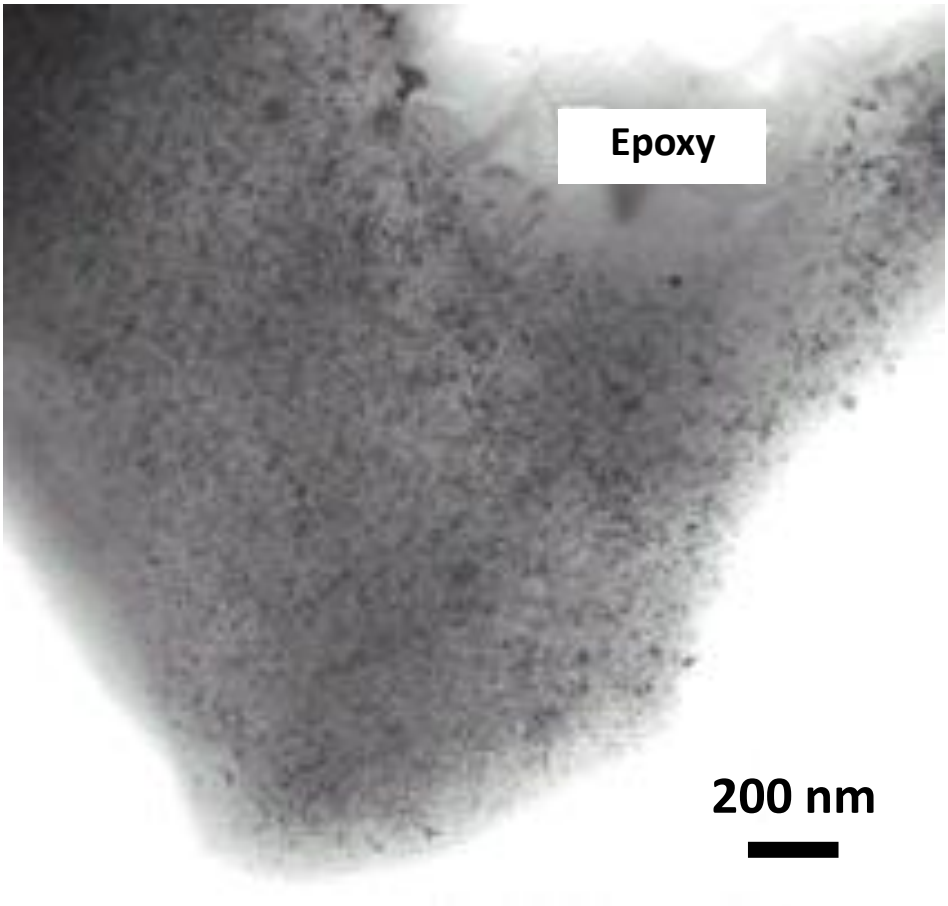
$$2Mg(g) + SiO_2(s) \Rightarrow 2MgO(s) + Si(s)$$

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

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- Selective dissolution of the MgO should then yield an interconnected, highly-porous Si replica of the starting SiO_2 template:

$$SiO_2 \Rightarrow 2MgO(s) + Si(s) \Rightarrow Si(s)$$

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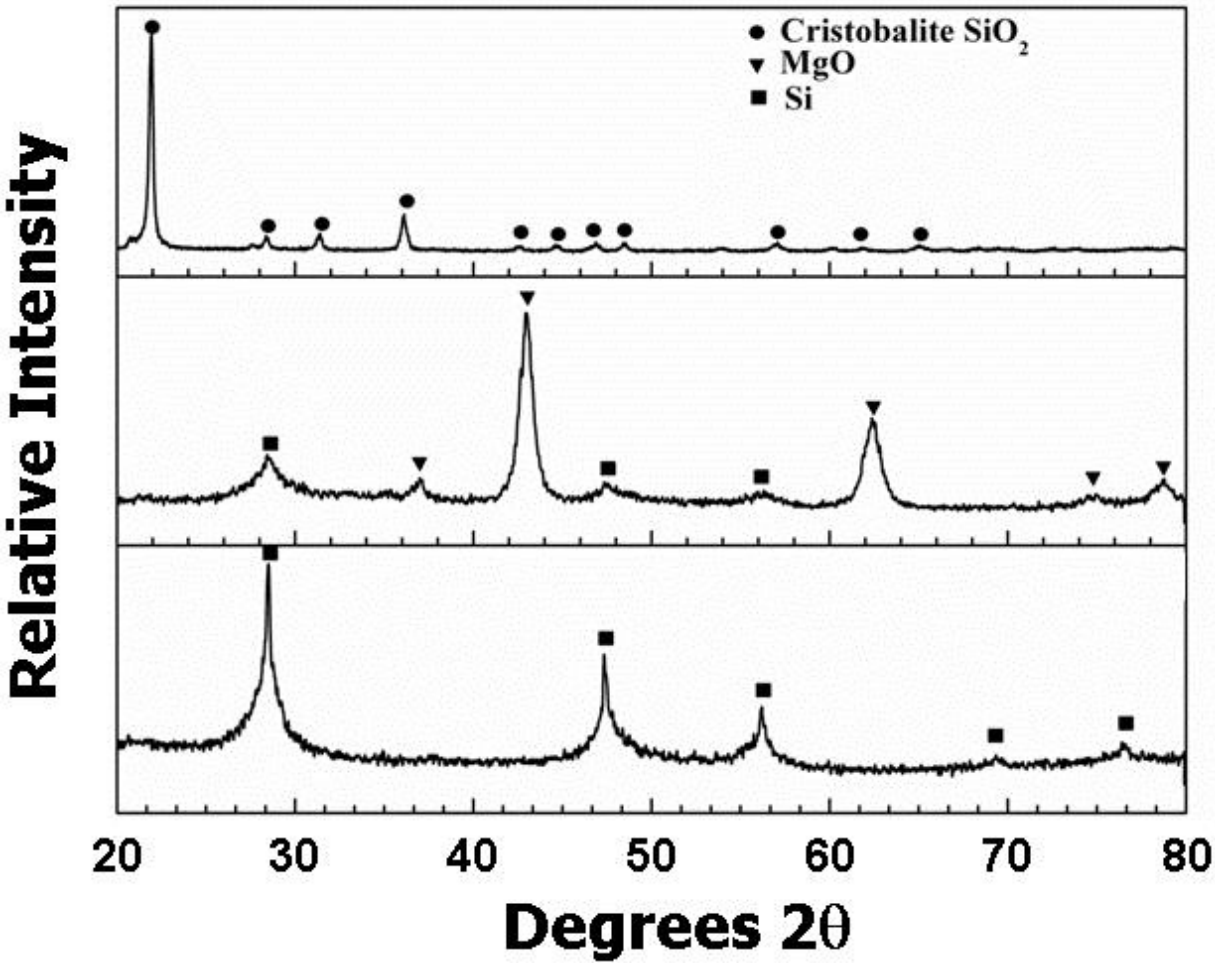
Conversion into Si-based Replicas



Starting Frustules

650°C, 2.5 h, $Mg:SiO_2$ = 2.5:1

1M HCl, 4 h

(average Si crystal size from Scherrer analysis = 8.1 nm)

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- Selective dissolution of the MgO should then yield an interconnected, highly-porous Si replica of the starting SiO_2 template:

$$SiO_2 \Rightarrow 2MgO(s) + Si(s) \Rightarrow Si(s)$$

$$\Delta V_m/V_m\ (SiO_2 \rightarrow Si) = -55.8 \text{ to } -58.5\%$$

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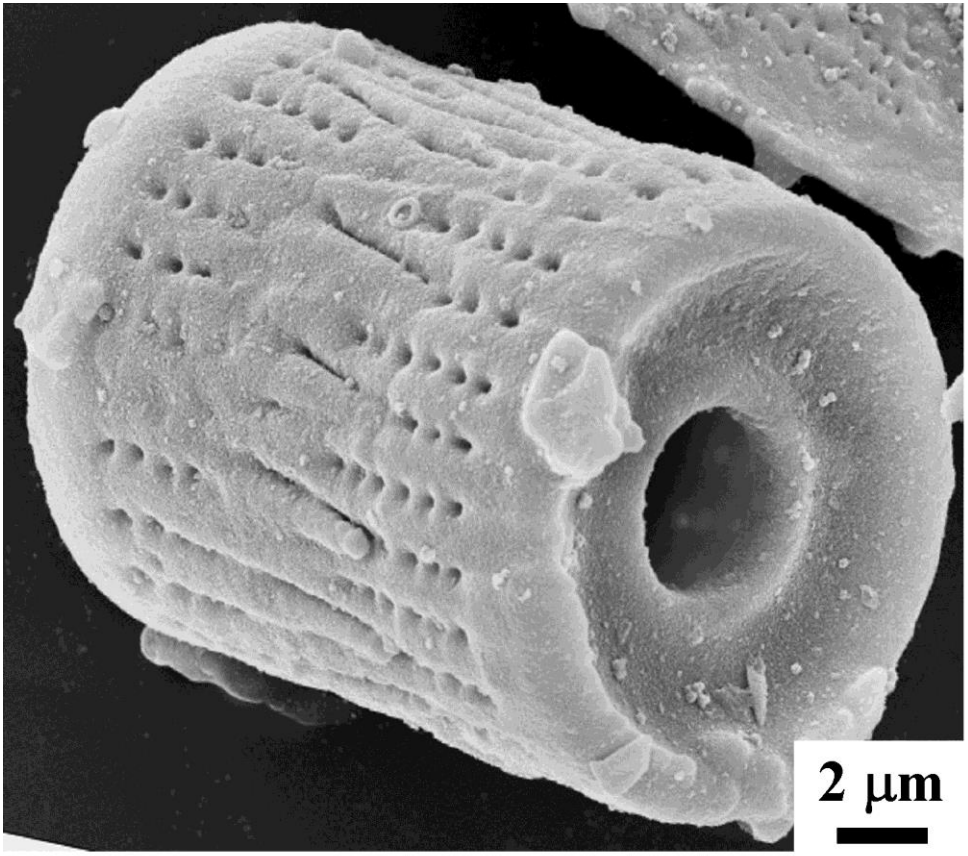
Conversion into Si Replicas



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

Secondary electron image

Surface Area: 541.0 m^2/g (BET analysis)

Z. Bao, et al., *Nature,* 446 [3] 172-175 (2007).

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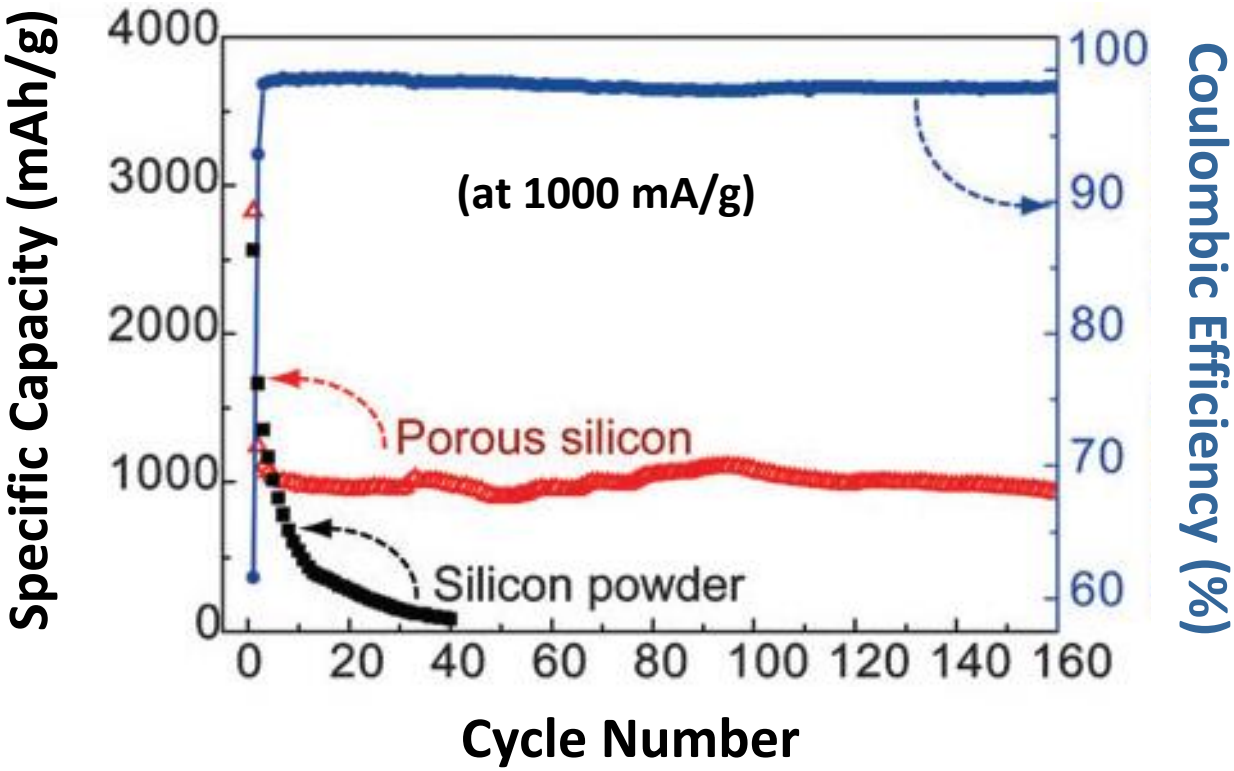
Porous Si for Lithium Ion Battery Anodes



p-Si μparticles:

- **SSA: 281 m^2/g**
- **Ave. crystal size: 10 nm**

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

A. Zing, J. Zhang, Z. Bao, Y. Mei, A.S. Gordin, K.H. Sandhage, *Chem. Commun.*, 49, 6743-6745 (2013).

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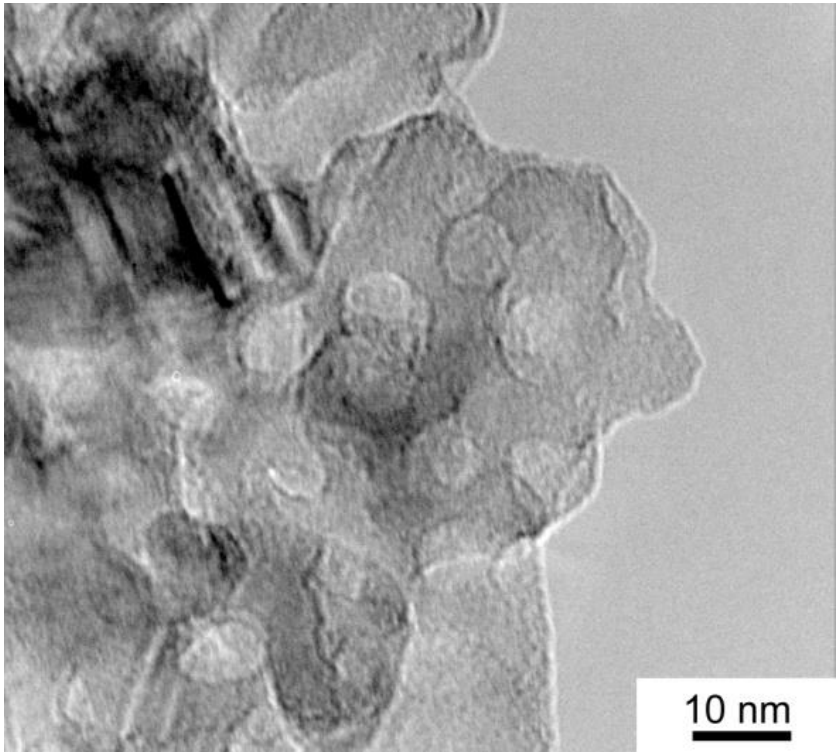
Porous Si for Lithium Ion Battery Anodes



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)

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Applications for Mg-derived Porous Si Replicas

- **Porous silicon anodes for lithium ion batteries**
  - L. Wu, et al., *ACS Appl. Mater. Interf.*, 8, 16862 (2016).
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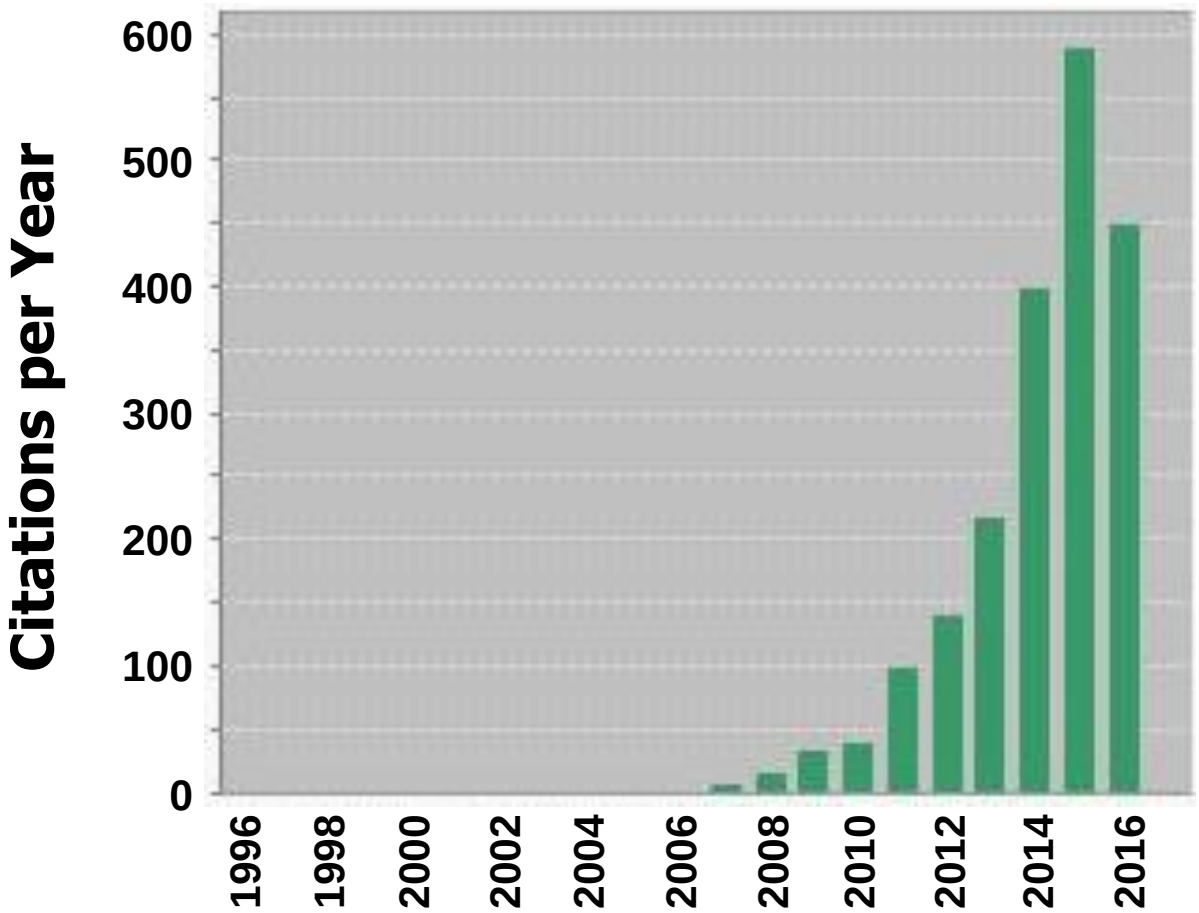
  - M. Waltzinger, et al., *Monat. Chem.*, 147, 269 (2016).

=> K. H. Sandhage, Z. Bao, *U.S. Patent No. 7,615,206*.

Applications for Mg-derived Porous Si Replicas

- **High-sensitivity sensors**
  - Z. Xia, et al., *Adv. Opt. Mater.*, 2, 235-239 (2014).
- **Thermoelectric particles**
  - M. L. Snedaker, et al., *Chem. Mater*, 25, 4867 (2013).
  - J. Szczech, et al., *J. Solid State Chem.*, 181, 1565 (2008).
- **Photoluminescent Particles**
  - Z. Bao, et al., *Nature,* 446, 172 (2007).
  - J. Zhu, J. Wu, Y. Wang, C. Meng, *J. Mater. Sci.*, 46, 7223 (2011).
- **Inverse Opals**
  - B. Hatton, et al., *PNAS*, 107, 10354 (2010).
  - F. Gallego-Gomez, et al., *Adv. Funct. Mater.*, 23, 5219 (2011).
- **Drug Delivery**
  - S. Maher, et al., *Adv. Funct. Mater.*, 25, 5107 (2015).
- **Photocathode**
  - S. Chandrasekaran, et al., *ACS Appl. Mater. Interf.*, 7, 17381 (2015).
  - B. H. Meekins, et al., *ACS Appl. Mater. Interf.*, 5, 2943 (2013).
- **Electromagnetic Wave Absorption**
  - S.-T. Liu, et al., *J. Magn. Magn. Mater.*, 394, 266 (2015).

Si via Magnesiothermic Reduction Citations



(Web of Science)

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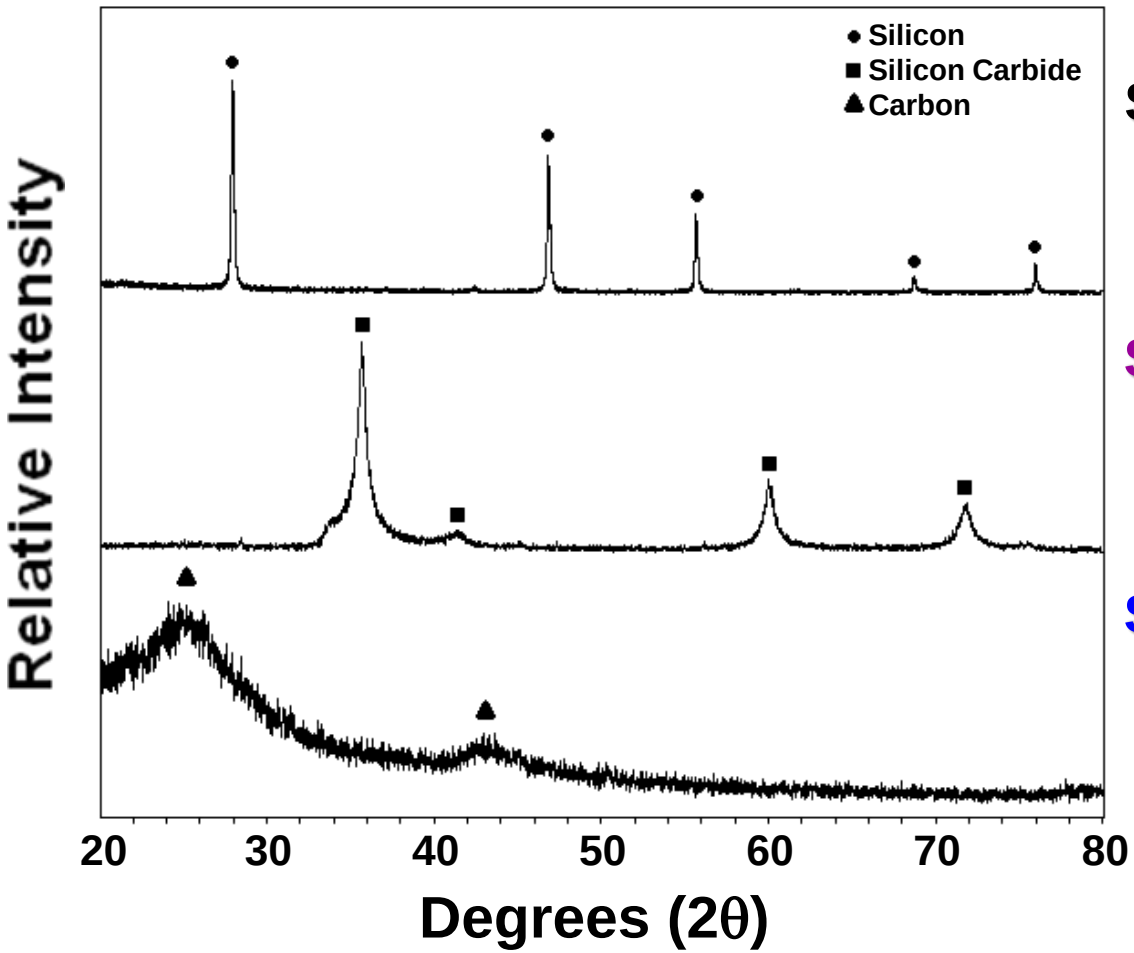
Reactive Conversion into SiC and C Replicas



$SiO_2 + Mg(g) \Rightarrow$

$2MgO + Si \Rightarrow Si$

$Si + CH_4(g) \Rightarrow$

$SiC + 2H_2(g)$

(1200°C, 12 h)

$SiC + 2Cl_2(g) \Rightarrow$

$C + SiCl_4(g)$

(950°C, 2 h)

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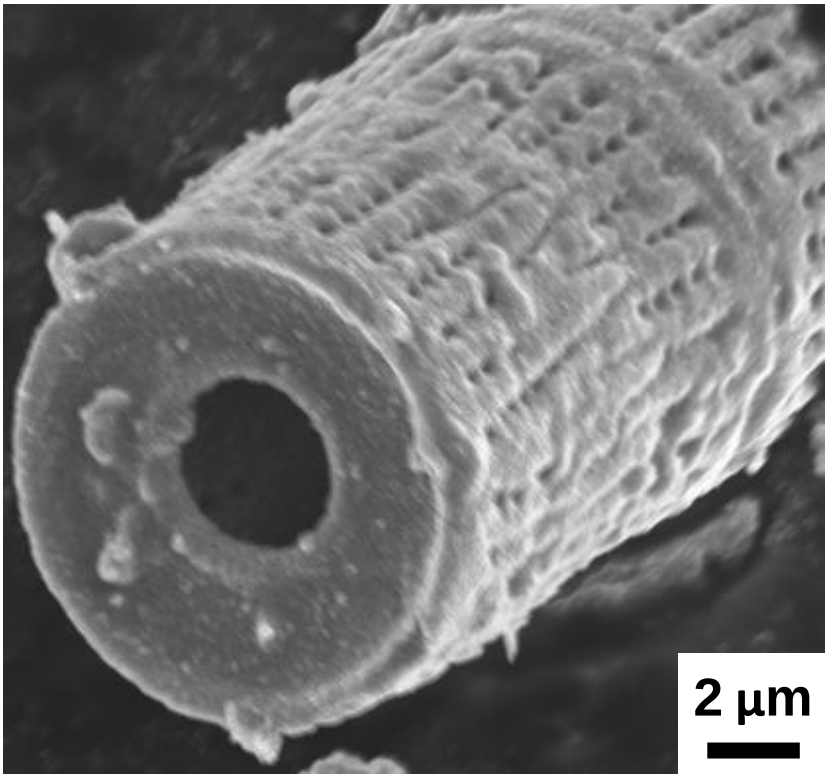
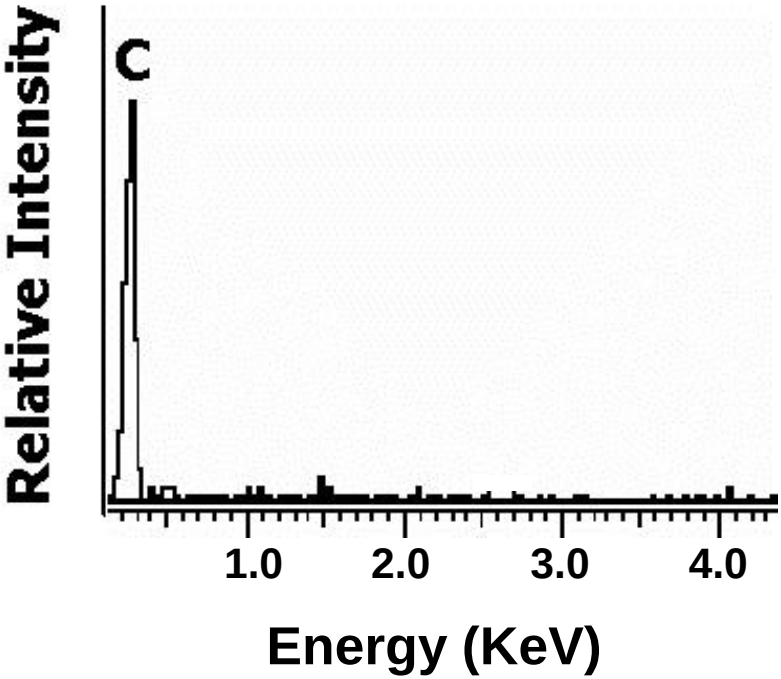
Reactive Conversion into Porous C Replicas



Secondary electron image



EDX analysis

BET Surface Area: 1,370 m^2/g!

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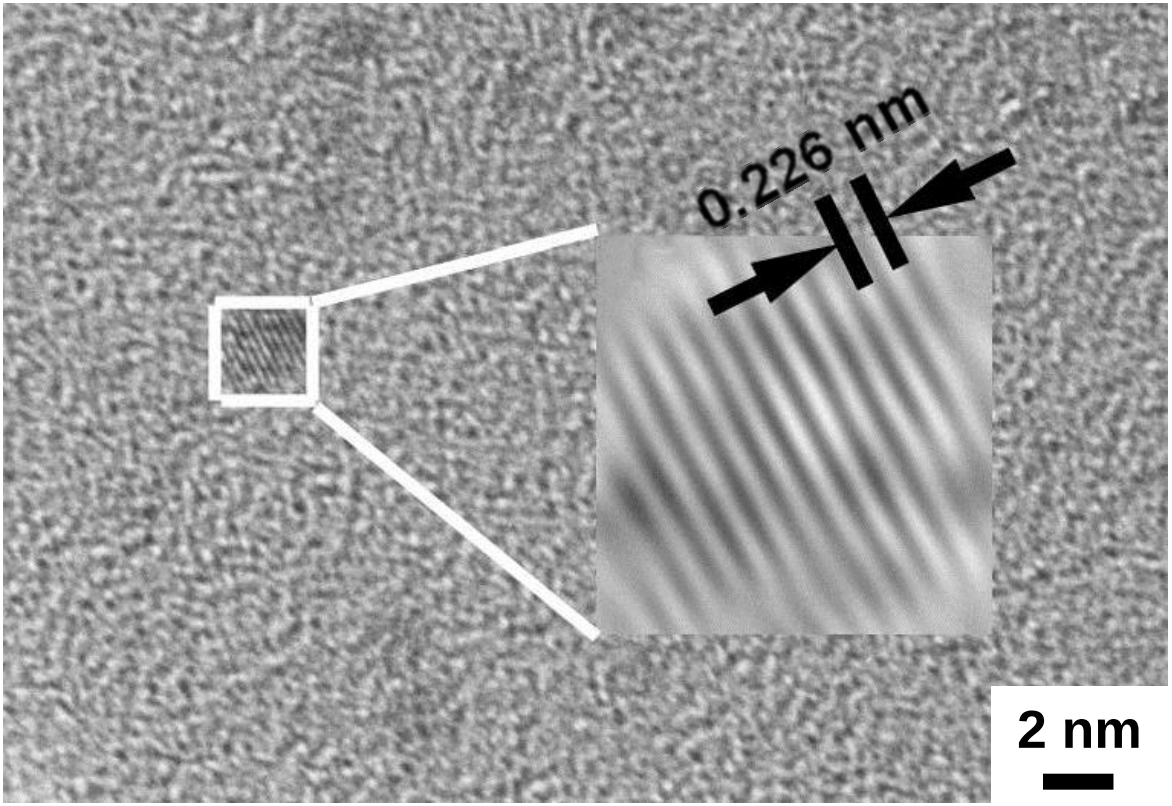
Pt Nanoparticles within C Frustule Replicas



HRTEM image

(Pt deposition from $Pt(CO)_2Cl_2$ vapor)

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PEM Fuel Cells and Oxygen Reduction

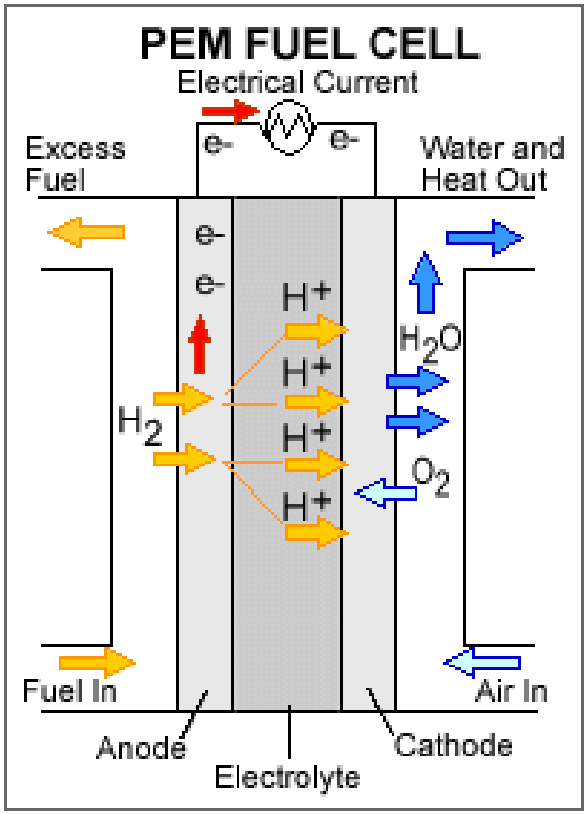
- At the anode of a proton exchange membrane (PEM) fuel cell, $H_2(g)$ is oxidized to yield protons and electrons:

$$H_2(g) \Rightarrow 2H^+ + 2e^-$$

- At the cathode, $O_2(g)$ undergoes following reduction reaction:

$$\tfrac{1}{2}O_2(g) + 2H^+ + 2e^- = H_2O$$

- The oxygen reduction reaction is relatively sluggish and significant R&D on catalysts and catalyst supports is underway.



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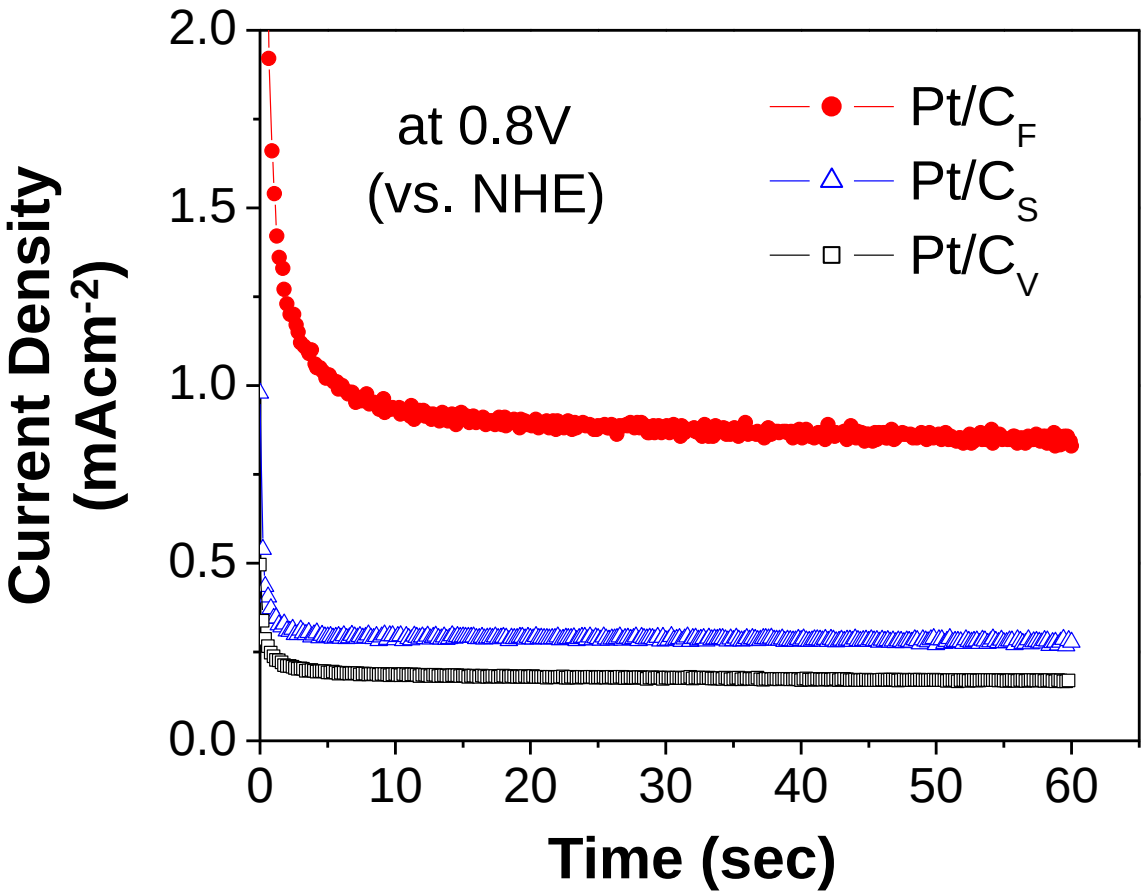
Catalysis of the Oxygen Reduction Reaction



(RDE, 2000 rpm, 0.5 M H_2SO_4 solution)

(with Prof. Meilin Liu, School of MSE, Georgia Tech)

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Surface Area, Pore Volume Analyses

Specimen	SSA (m^2g^{-1})	SMiV (cm^3g^{-1})	SMeV (cm^3g^{-1})
C_F	1370	0.282	1.53
C_V	227	0.0232	0.413
C_S	1230	0.286	1.40

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

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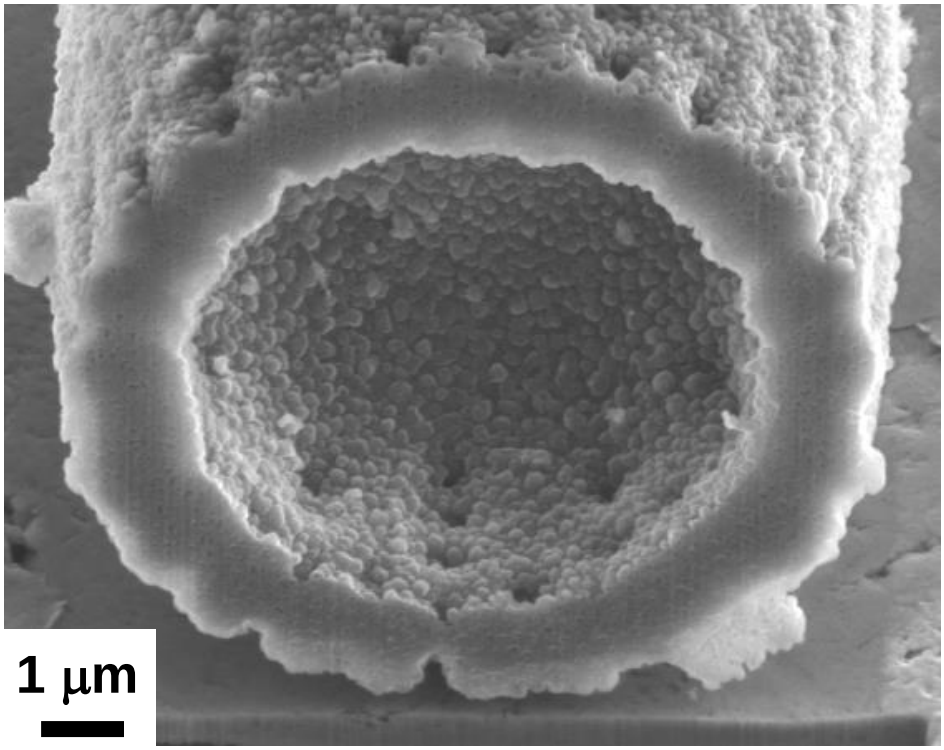
Carbon Diatom Frustule Replica



Secondary electron image after partial FIB milling

Hollow frustule replicas => short diffusion distance for oxygen! (half wall thickness ~ 700 nm)

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