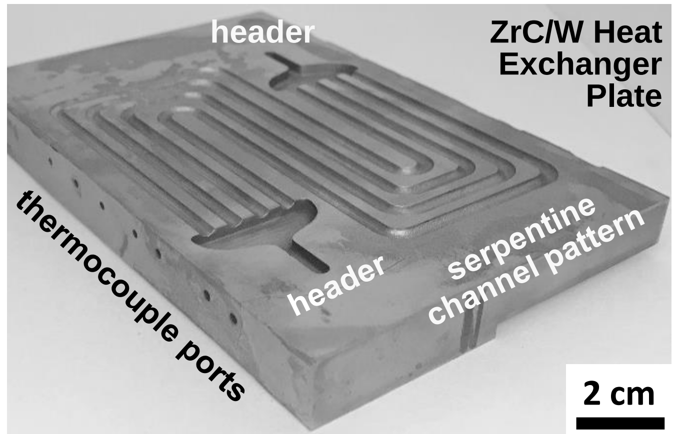
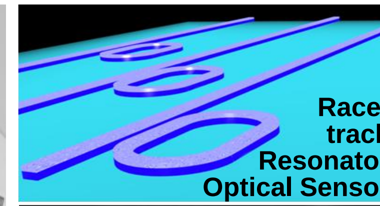
Shape-Preserving Transformation of Synthetic & Biogenic Structures into Chemically-Tailored 3-D Macroscopic and Microscopic Materials





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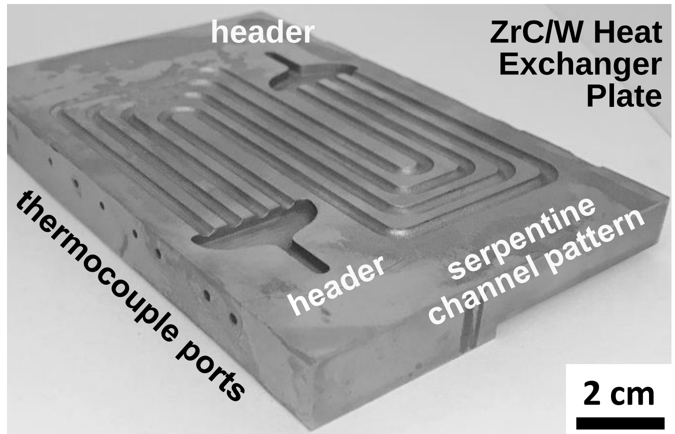
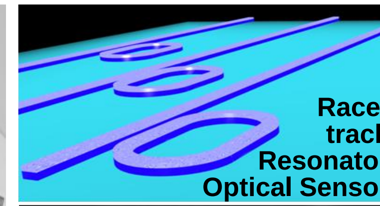
Materials Alchemy





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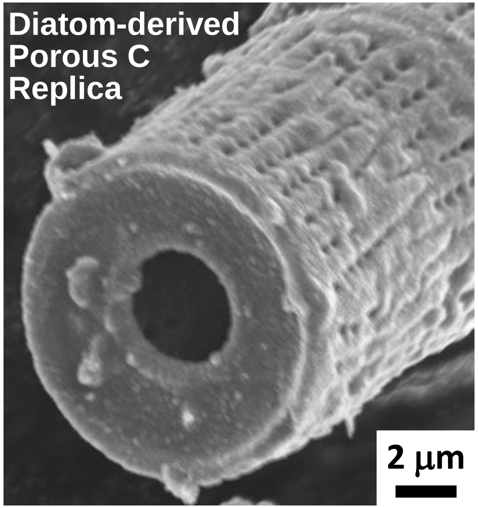
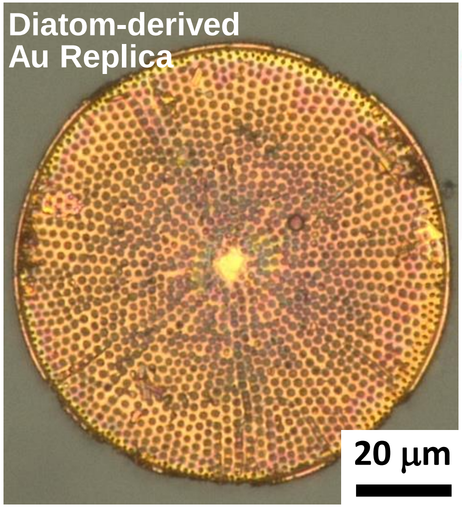
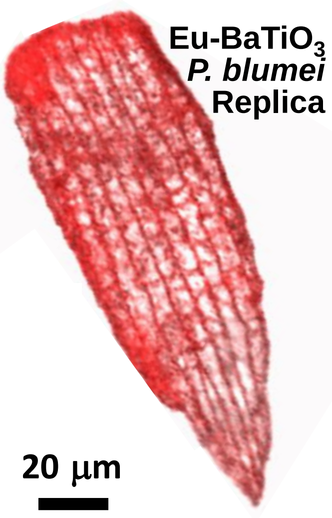
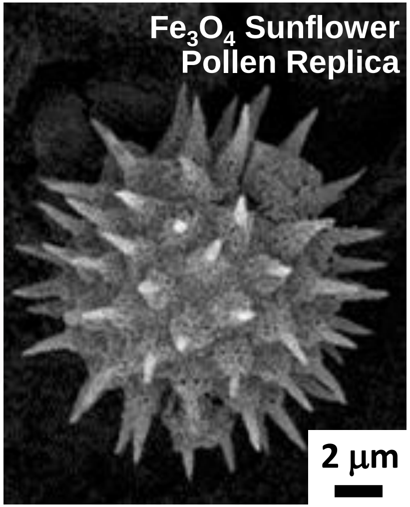
Materials Alchemy









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Research Colleagues (partial list)

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Brandon Goodwin[1,5]
Ari Gordin[1]
SungHwan Hwang[3]
Jiaqi Li[3]
Naotaka Ogura[3]
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Supattra Singnisai[3]
Alex R. Strayer[3]
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Jonathan Vernon[1,4]

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Yunnan Fang[1]
Greg Itskos[3]
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Meysam Tabandeh-Khorshid[3]

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Joanna Aizenberg[6]
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Asegun Henry[1,7]
Mark Hildebrand[8]
Nils Kröger[1,9]
Meilin Liu[1]
Seth Marder[1]
Carson Meredith[1]
Rajesh Naik[4]
Joe Perry[1]
Devesh Ranjan[1]

[1]Georgia Institute of Technology; [2]Tongji University; [3]Purdue University; [4]Air Force Research Laboratory/Wright Patterson Air Force Base; [5]Fisk University; [6]Harvard University; [7]Massachusetts Institute of Technology; [8]Scripps Institution of Oceanography; [9]TU Dresden

Shape-Preserving Chemical Transformation

- **Fluid/Solid Reactions (displacement, additive, subtractive)**
  - **Macroscale/microstructured inorganic templates (liquid/solid reactions)**
  - **Microscale/nanostructured inorganic templates (gas/solid reactions)**
- **Conformal Coating (inorganic, organic templates)**
  - **Surface sol-gel-based oxide deposition**
  - **Protein-enabled oxide and oxide/organic deposition**
  - **Electroless metal deposition**

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Shape-Preserving Chemical Transformation

- Fluid/Solid Reactions (displacement, additive, subtractive)
  - Macroscale/microstructured inorganic templates (liquid/solid reactions)
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- Conformal Coating (inorganic, organic templates)
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  - Electroless metal deposition

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Displacive Compensation of Porosity (DCP) Process

(U.S. Patents No. 6,833,337; No. 6,598,656; No. 6,407,022)

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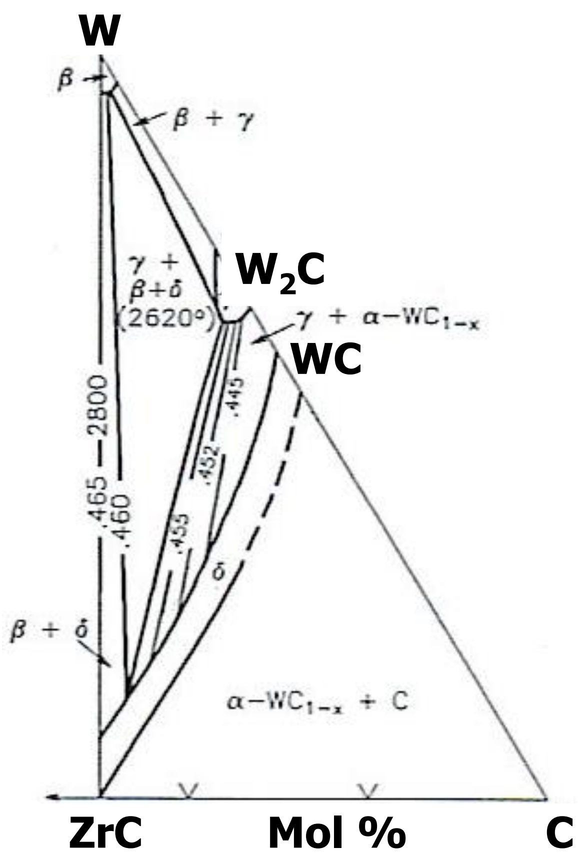
ZrC/W Composites

- T_m: W = 3422°C, ZrC_{1-x} ≤ 3445°C (T_{sol} = 2800°C)
- Chemical compatibility
  (No intermediate compounds; limited solubilities)



V. N. Eremenko, et al., C-W-Zr System (Fig. 9034) in *Phase Diagrams for Ceramists*, Vol. X, Ed. A. E. McHale, The American Ceramic Society, 1994.

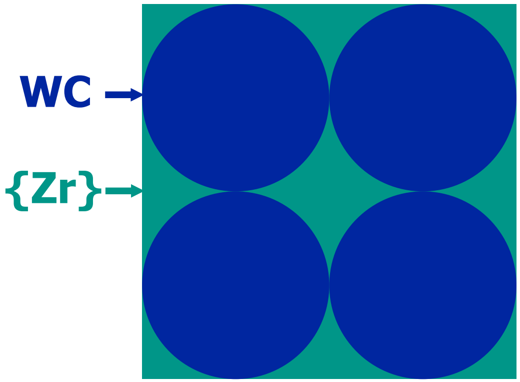
ZrC/W Composites

- T_m: W = 3422°C, ZrC_{1-x} ≤ 3445°C (T_{sol} = 2800°C)
- Chemical compatibility
  (No intermediate compounds; limited solubilities)
- Thermal compatibility!
  (CTE W: 4.5 to 9.2X10^{-6}/°C from RT to 2700°C
  ZrC: 4.0 to 10.2X10^{-6}/°C from RT to 2700°C
  Thermal Conductivity: W: 114-93 W/mK
  (1000-2200°C) ZrC: 35-49 W/mK)
- Mechanical compatibility
  (ZrC is hard and erosion-resistant at >2000°C,
  whereas W exhibits B->D transition at ≤400°C)
- Reduced weight
  (ρ(ZrC) = 6.63 g/cm³ vs. ρ(W) = 19.3 g/cm³)

=> **attractive for solid-fueled rocket nozzles**

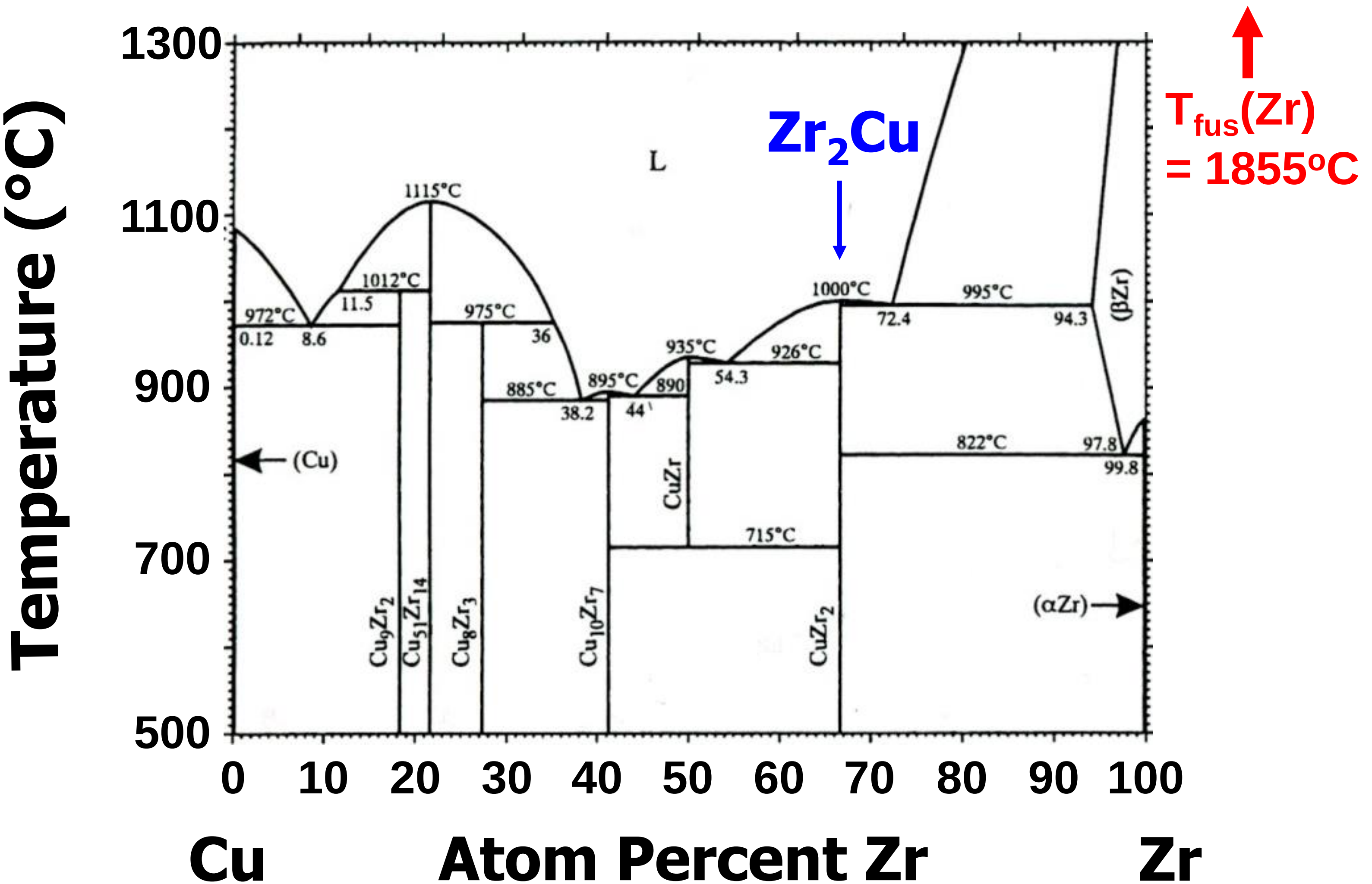
Displacive Compensation of Porosity

$WC(s) + \{Zr\}$



Infiltrated

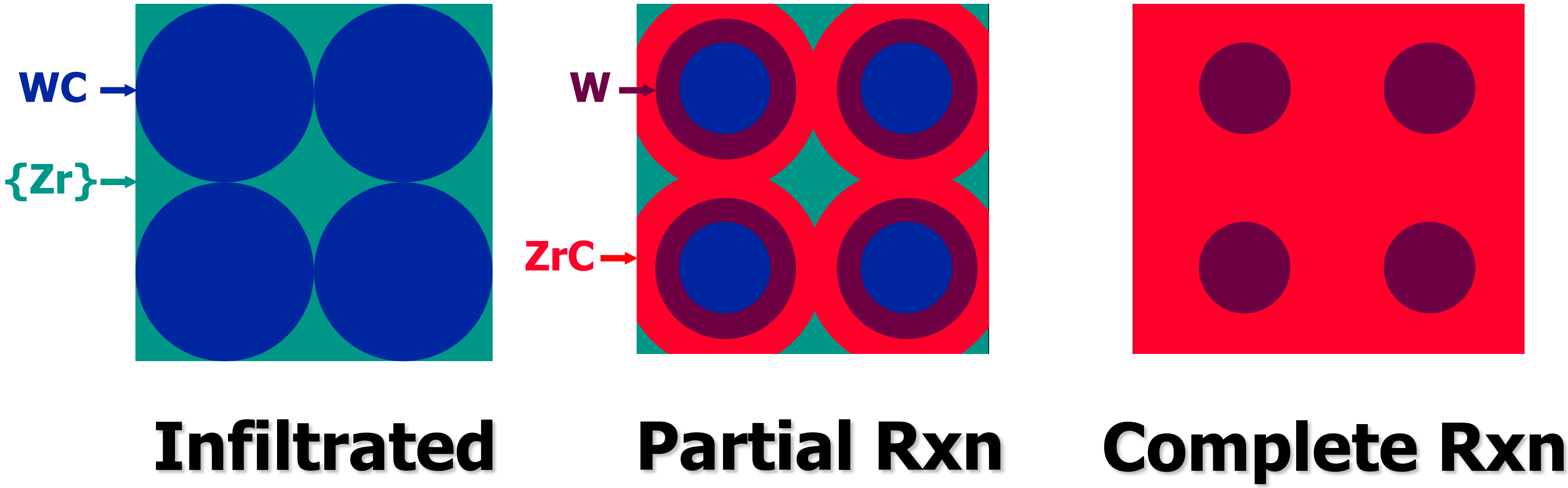
Zr-Cu Phase Diagram



Displacive Compensation of Porosity

$WC(s) + \{Zr\} \Rightarrow ZrC(s) + W(s)$

where $V_m[ZrC + W] = 2.01V_m[WC]$



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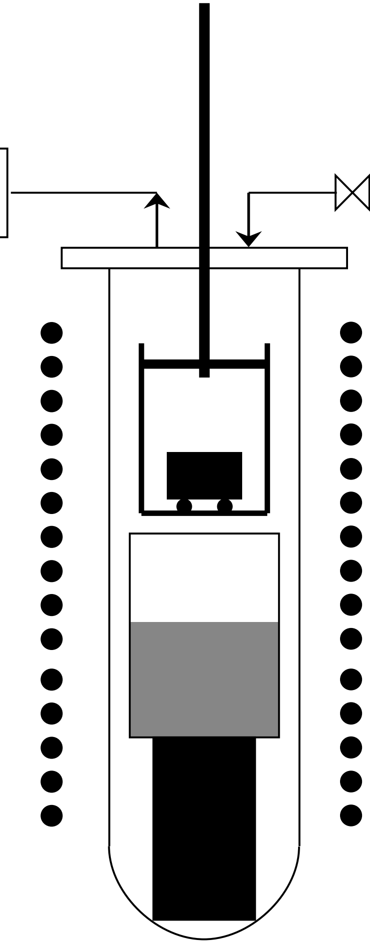
Reactive Infiltration

Inert atmosphere infiltration system



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DCP Conversion of CNC-Machined Nozzle

CNC machined, porous WC Nozzle

After infiltration, DCP reaction

After removal of adhering Cu

(Infiltration with Zr_2Cu(l) at 1150^{o}C/30 min, then further reaction at 1300^{o}C/2 h)

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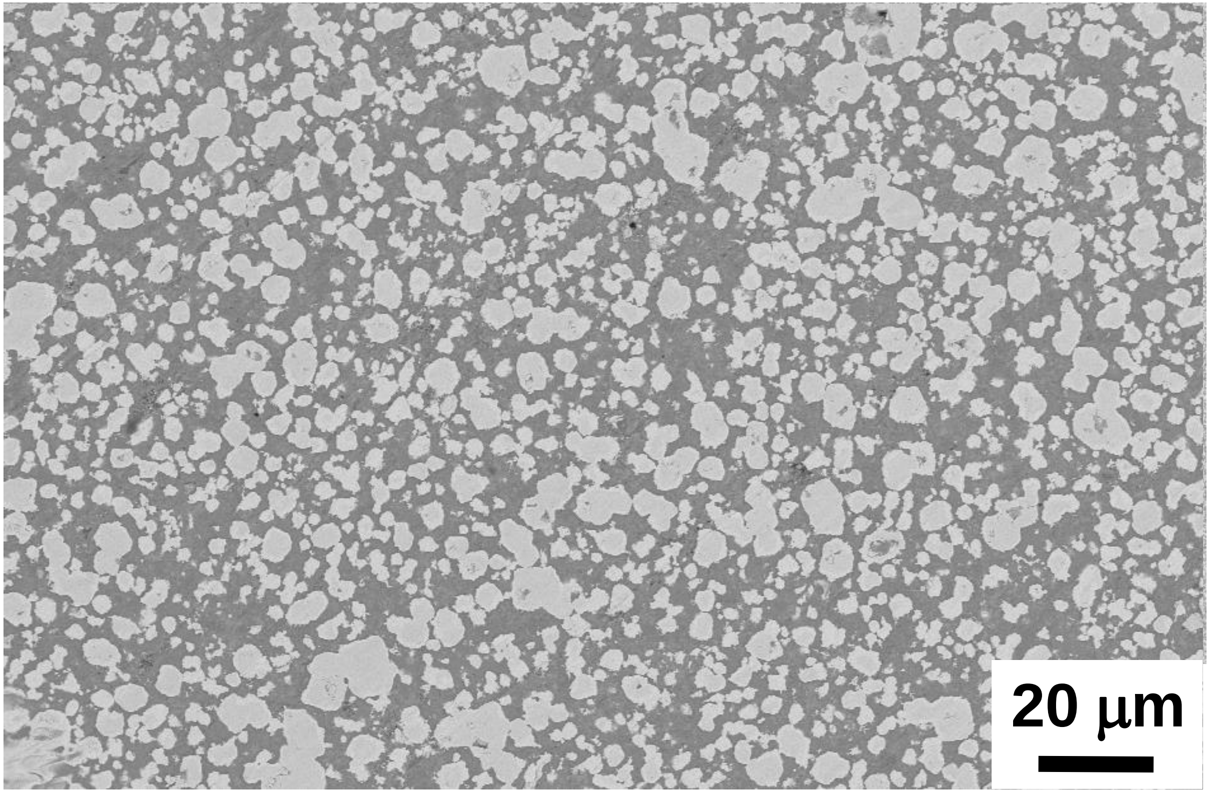
DCP Conversion of CNC-Machined Nozzle

Specimen	Nozzle Exit Outer Diameter	Nozzle Entrance Outer Diameter	Nozzle Height
WC Nozzle Preform	50.65$\pm$0.09 mm	37.50$\pm$0.08 mm	32.13$\pm$0.22 mm
ZrC/W-based Nozzle	50.32$\pm$0.16 mm	37.23$\pm$0.07 mm	32.00$\pm$0.30 mm

$\Delta D/D_o$: -0.6$\pm$0.1% $\Delta D/D_o$: -0.7$\pm$0.1% $\Delta H/H_o$: -0.4$\pm$0.2%

DCP-Converted ZrC/W-based Composite



Backscattered electron image

(Infiltration with Zr_2Cu(l) at 1150°C/30 min, then further reaction at 1300°C/2 h)

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Rigid, Porous Gel-Cast WC Preforms

Solid Fuel Rocket Nozzles

- **Temperatures in excess of 2500ºC in a few secs**
- **Al_2O_3(l) and gas products traveling at supersonic speeds (≥2,500 m/s).**
- **New materials that are:**
  - **high melting**
  - **thermal shock resistant**
  - **erosion resistant**
  - **lightweight**
  - **non-porous**
  - **inexpensive (raw material, nozzle fabrication)**

are needed.

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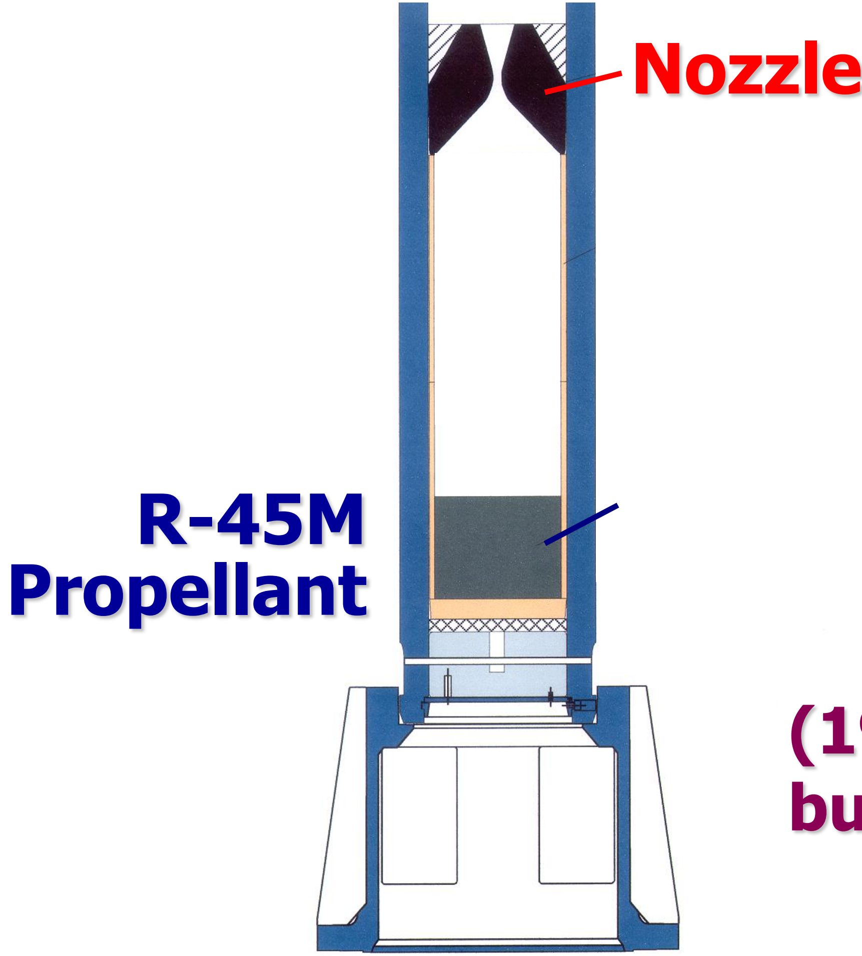
ZrC/W-based Rocket Nozzle Inserts

($\Delta D/D_o$ = -0.5±0.3%: 9.63 to 9.65 cm,
3.03 to 3.05 cm)

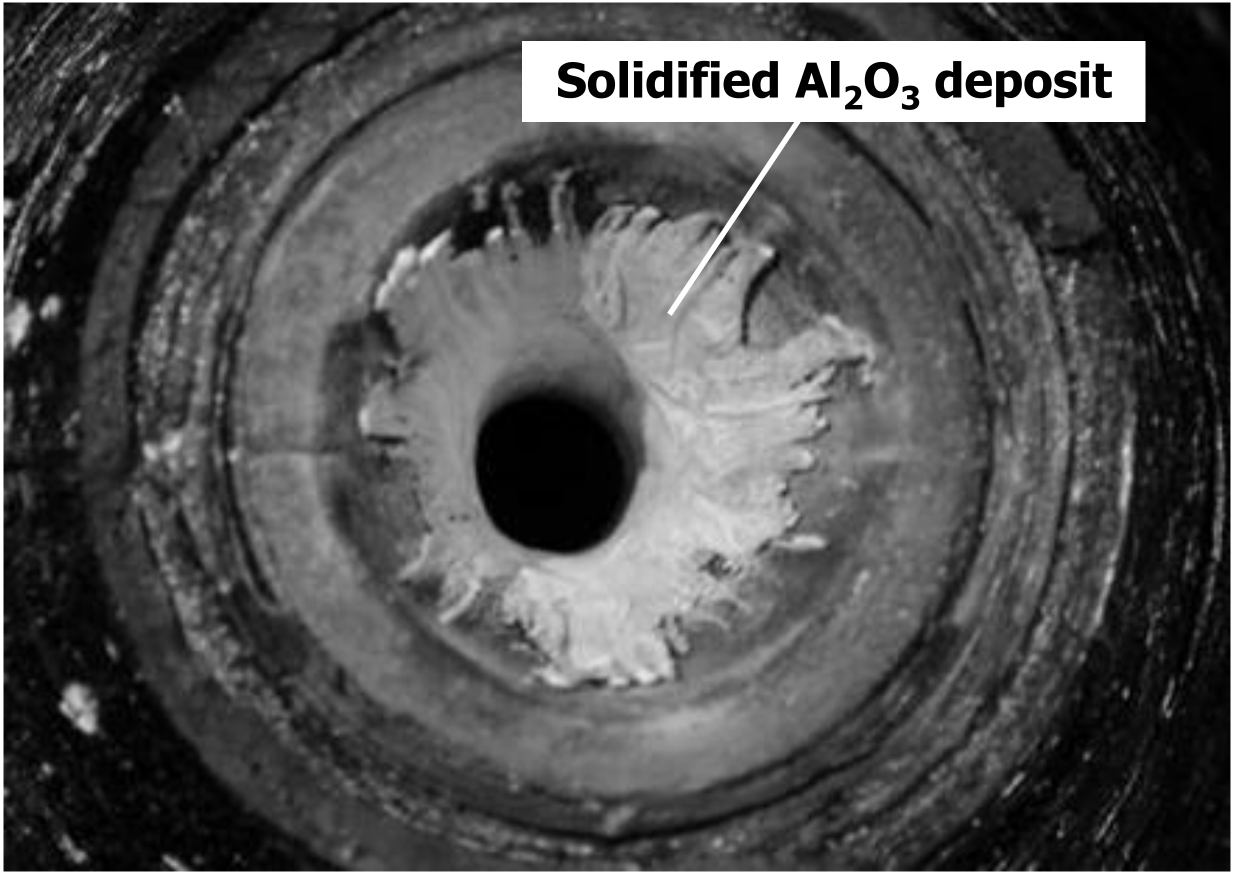
Pi-K Rocket Nozzle Test (Edwards AFB)



(19 wt% Al propellant, burn pressure = 3.5 MPa)

(with Wes Hoffman, EAFB)

Pi-K Rocket Nozzle Test (Edwards AFB)



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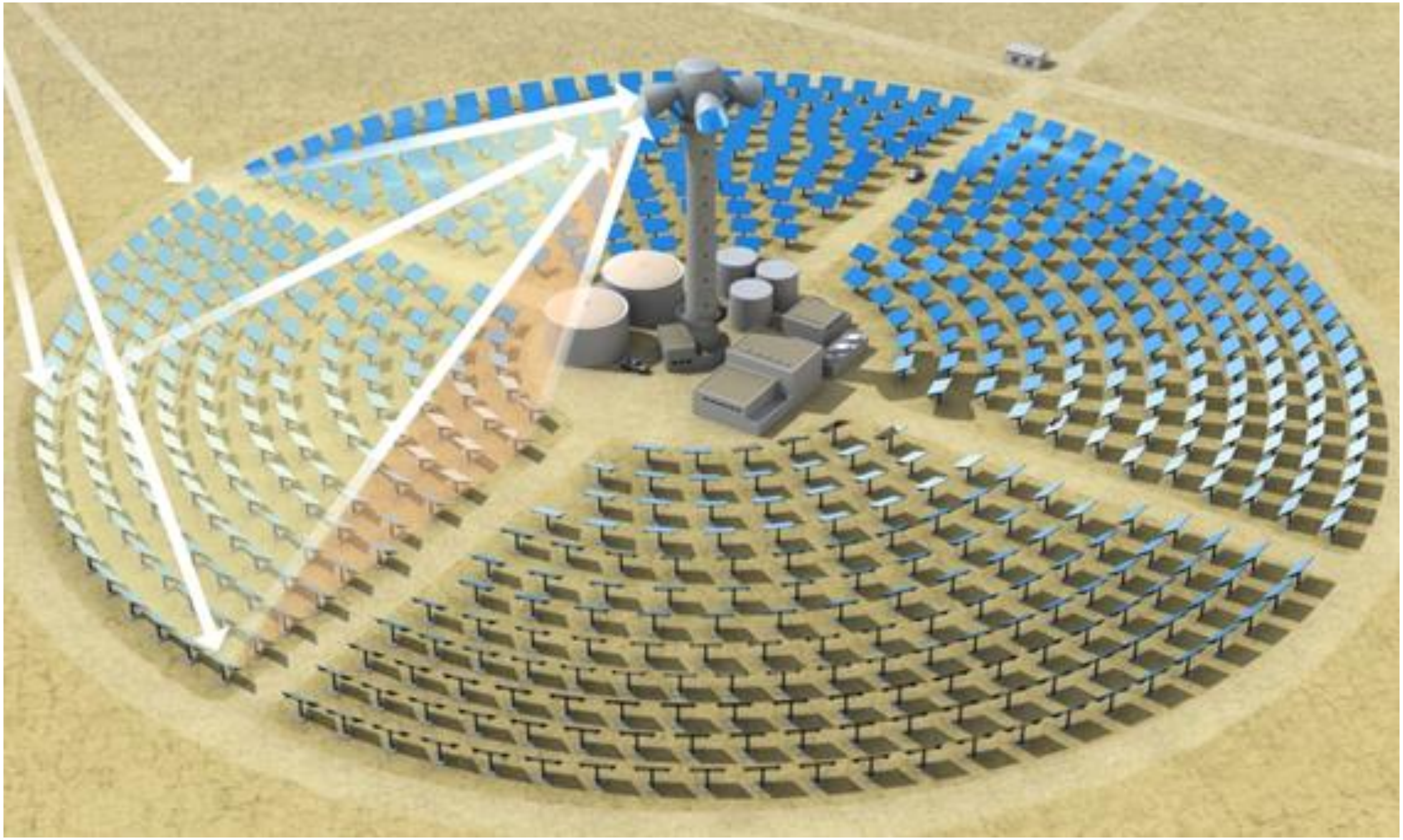
Processing and Properties of Robust Ceramic/Metal Composites for <u>Heat Exchangers</u> Operating at $\underline{>}750^{o}$C with Supercritical CO_2

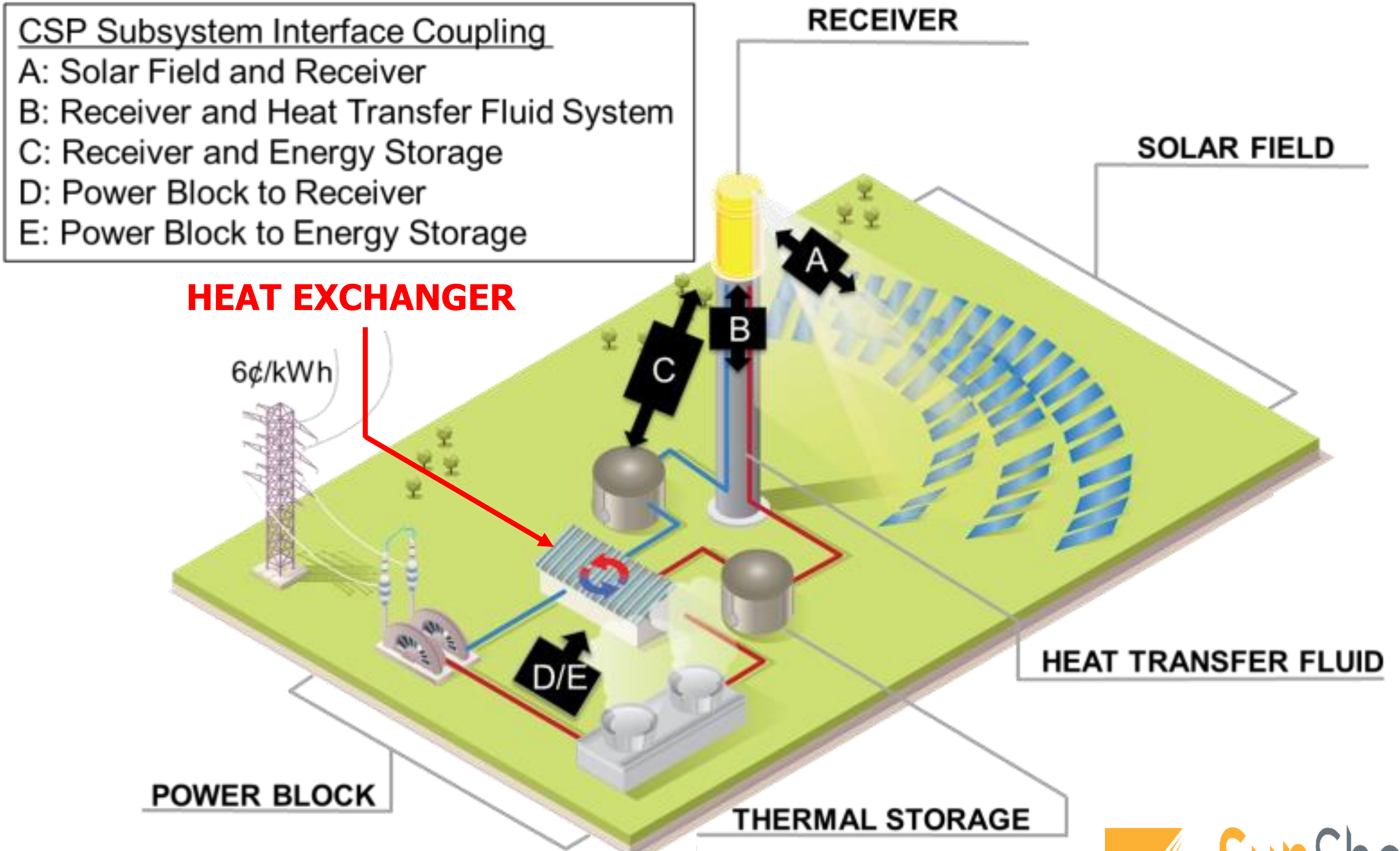
Mario Caccia[1], Meysam Tabandeh-Khorshid[1], Grigoris Itskos[1], Alex R. Strayer[1], Supattra Singnisai[1], Adam S. Caldwell[1], Andrew Rohskopf[2], Anthony M. Schroeder[3], Andres M. Rossy[4], Dorrin Jarrahbashi[2], Taegyu Kang[2], Sandeep Pidaparti[2], Seshadev Sahoo[1], Edgar Lara-Curzio[4], Mark H. Anderson[3], Asegun Henry[2], Devesh Ranjan[2], <u>Kenneth H. Sandhage</u>[1]

[1] School of Materials Engineering, Purdue University, W. Lafayette, IN USA
[2] School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA USA
[3] Department of Engineering Physics, University of Wisconsin, Madison, WI USA
[4] Division of Materials Science and Technology, Oak Ridge National Laboratory, Oak Ridge, TN USA

The Power Tower Concept for Concentrated Solar Power

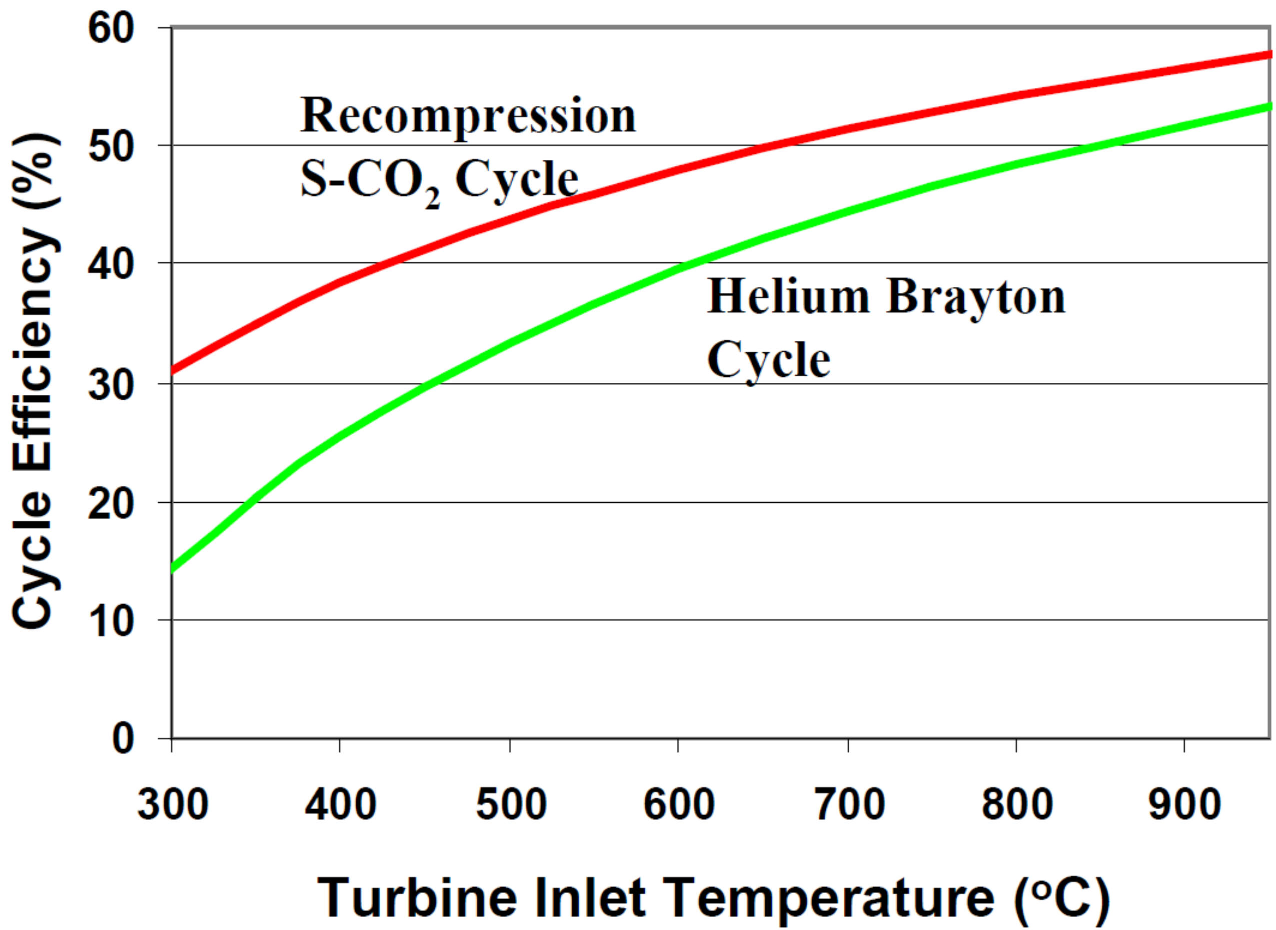


Concentrated Solar Power Tower



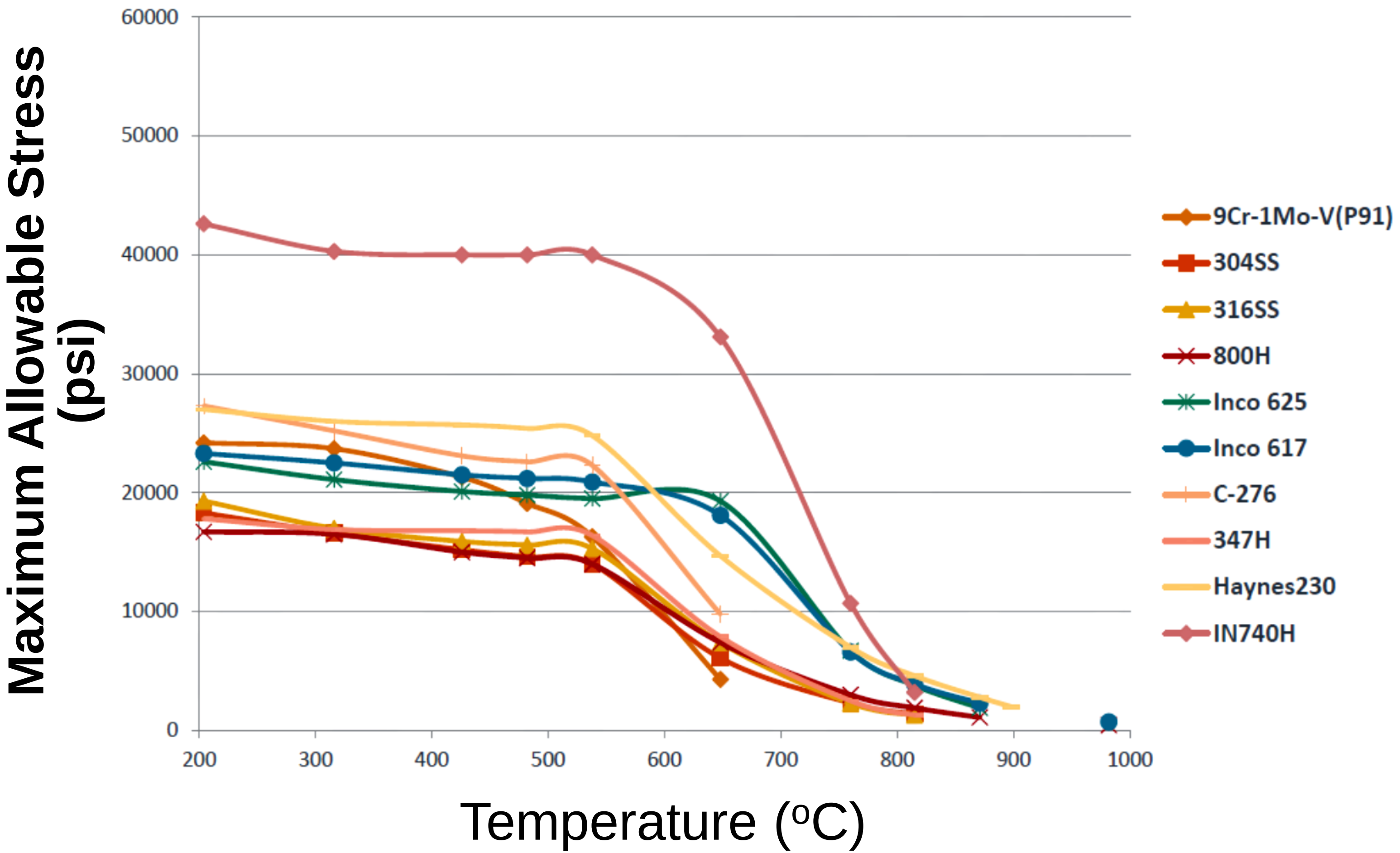
SunShot
U.S. Department of Energy

Push for Higher Turbine Inlet Temperatures



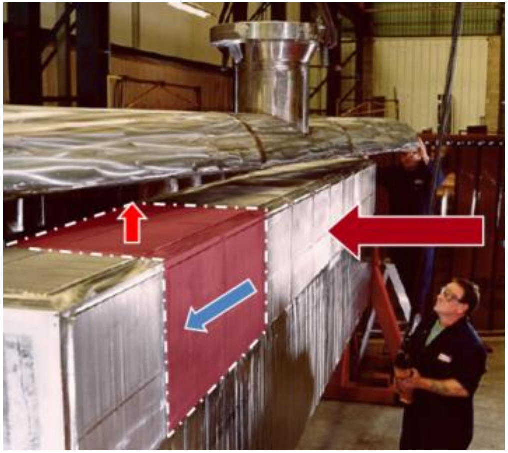
V. Dostal, M. J. Driscoll, P. Hejzlar, N. E. Todreas, "A Supercritical CO_2 Gas Turbine Power Cycle for Next-Generation Nuclear Reactors," *Proc. 10th Intl. Conf. Nuclear Engineering*, ICONE 10, Arlington, VA, 2002; V. Dostal, P. Hejzlar, M. J. Driscoll, "The Supercritical Carbon Dioxide Power Cycle: Comparison to Other Advanced Cycles," *Nuclear Technol.*, 154, 283-301 (2006).

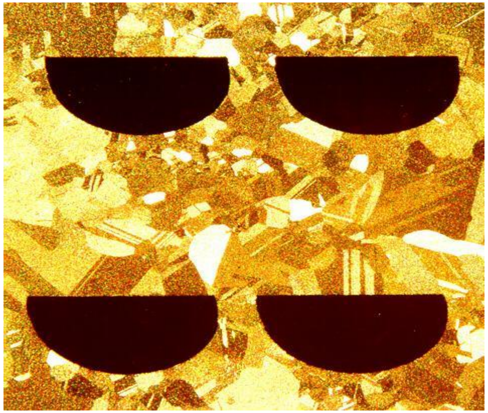
State of the Art: Metal Alloy Printed Circuit HEXs



2010 ASME Boiler Pressure Vessel Code, Sec. II, from Tables 1A and 1B, July 1, 2010, New York, NY (compiled by Mark Anderson)

An Attractive Alternative: ZrC/W HEXs





D. Southall, S.J. Dewson, *Proc. ICAPP '10*, San Diego, CA, 2010; R. Le Pierres, et al., *Proc. SCO_2 Power Cycle Symposium 2011*, Boulder, CO, 2011; D. Southall, et al., *Proc. ICAPP '08*, Anaheim, CA, 2008.

Current Technology:

- **Printed Circuit HEXs: patterned etching of metallic alloy plates, then diffusion bonding**
- **Metal alloy mechanical properties degrade significantly above 650^{o}C**

New Technology*:

- **ZrC/W HEXs: mechanical forming of channeled porous WC plates, conversion into dense net-size ZrC/W plates, then diffusion bonding**
- **Higher strength, higher stiffness, and higher thermal conductivity at ≥750^{o}C**

***A. Henry, K. H. Sandhage, PCT/U.S. Patent Application**

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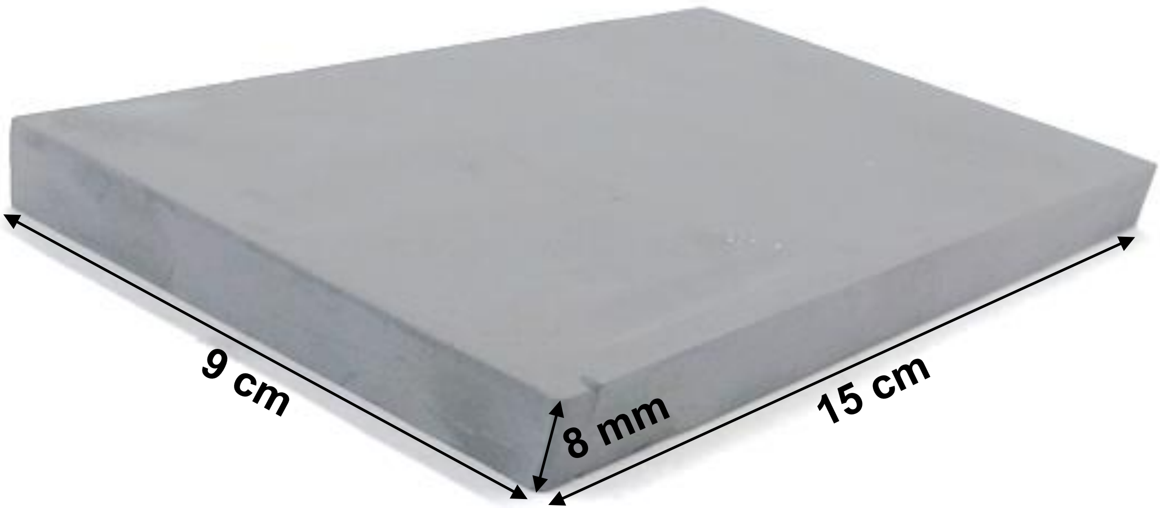
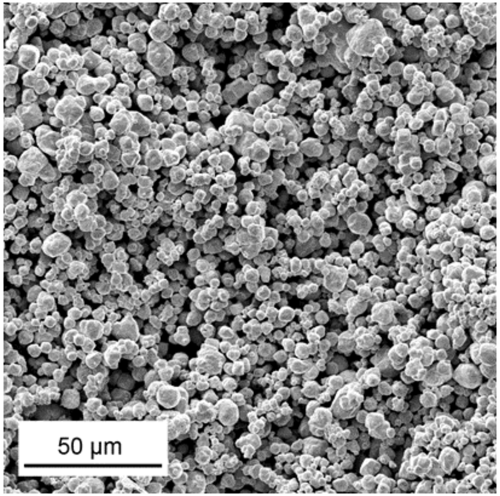
Manufacturing ZrC/W HEXs

Fabricate pairs of porous WC preform plates (one with patterned channels)



Porous WC Preform Plate (after powder compaction, light sintering at 1400°C/2 h)



SE image of fracture section

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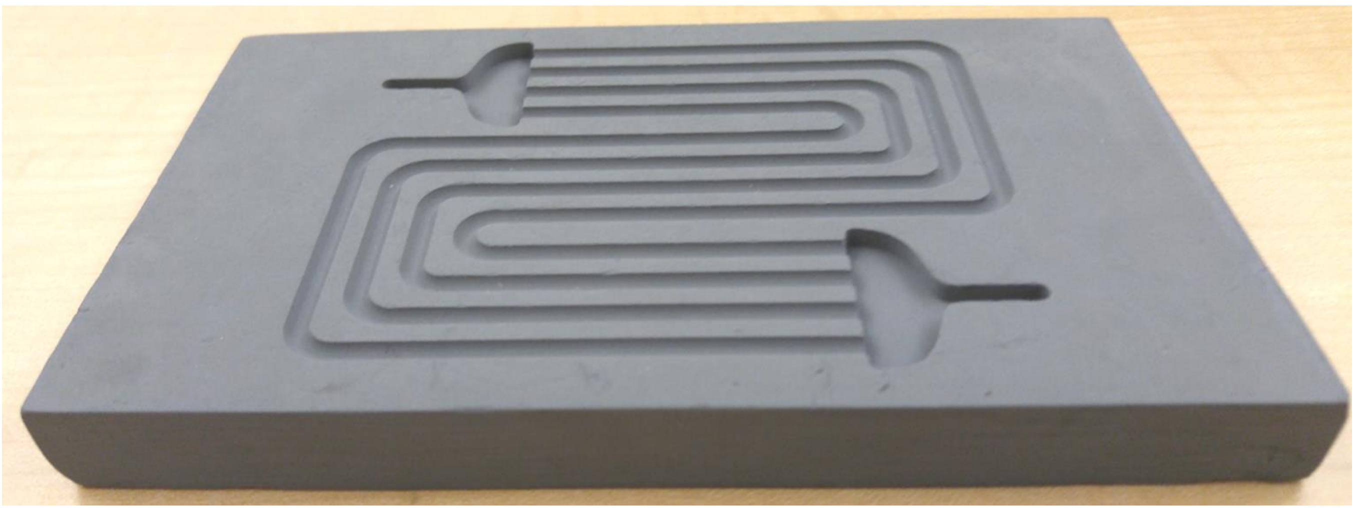
Manufacturing ZrC/W HEXs

Fabricate pairs of porous WC preform plates (one with patterned channels)



Green Machined Porous WC Preform Plates

"Ceramic-metal composites for heat exchangers in concentrated solar power plants," M. Caccia, M. Tabandeh-Khorshid, G. Itskos, A. R. Strayer, A. S. Caldwell, S. Pidaparti, S. Singnisai, A. D. Rohskopf, A. M. Schroeder, D. Jarrahbashi, T. Kang, S. Sahoo, N. R. Kadasala, A. Marquez-Rossy, M. H. Anderson, E. Lara-Curzio, D. Ranjan, A. Henry, K. H. Sandhage, *Nature*, 562 (7727) 406-409 (2018).

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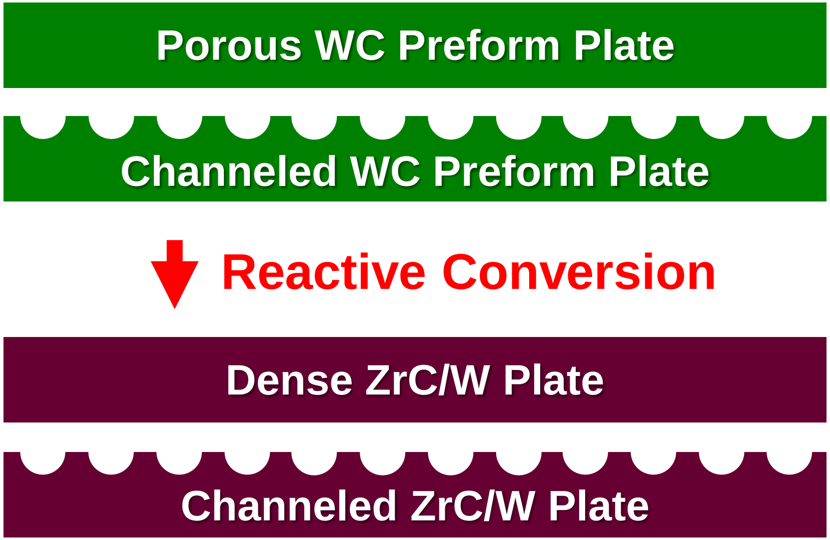
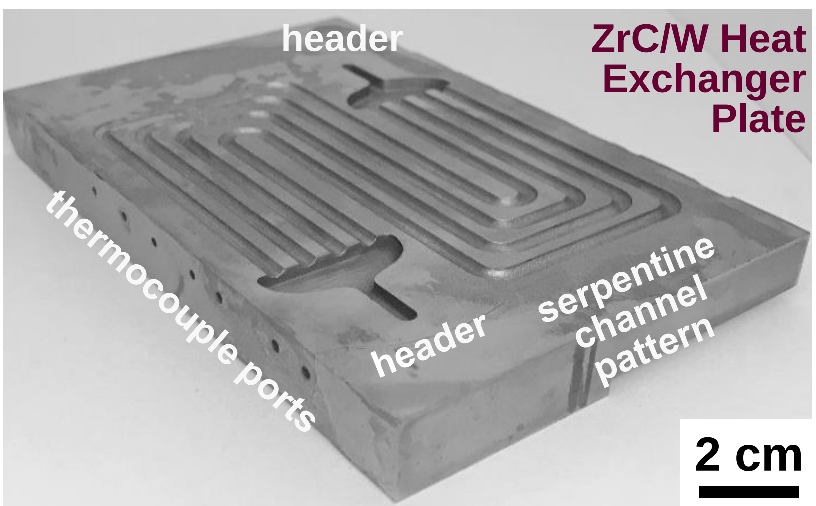
Manufacturing ZrC/W HEXs



Fabricate pairs of porous WC preform plates (one with patterned channels)

Generate net-shape/size dense ZrC/W plates via patented DCP process



M. Caccia, M. Tabandeh-Khorshid, G. Itskos, A. R. Strayer, A. S. Caldwell, S. Pidaparti, S. Singnisai, A. D. Rohskopf, A. M. Schroeder, D. Jarrahbashi, T. Kang, S. Sahoo, N. R. Kadasala, A. Marquez-Rossy, M. H. Anderson, E. Lara-Curzio, D. Ranjan, A. Henry, K. H. Sandhage, *Nature*, 562 (7727) 406-409 (2018).

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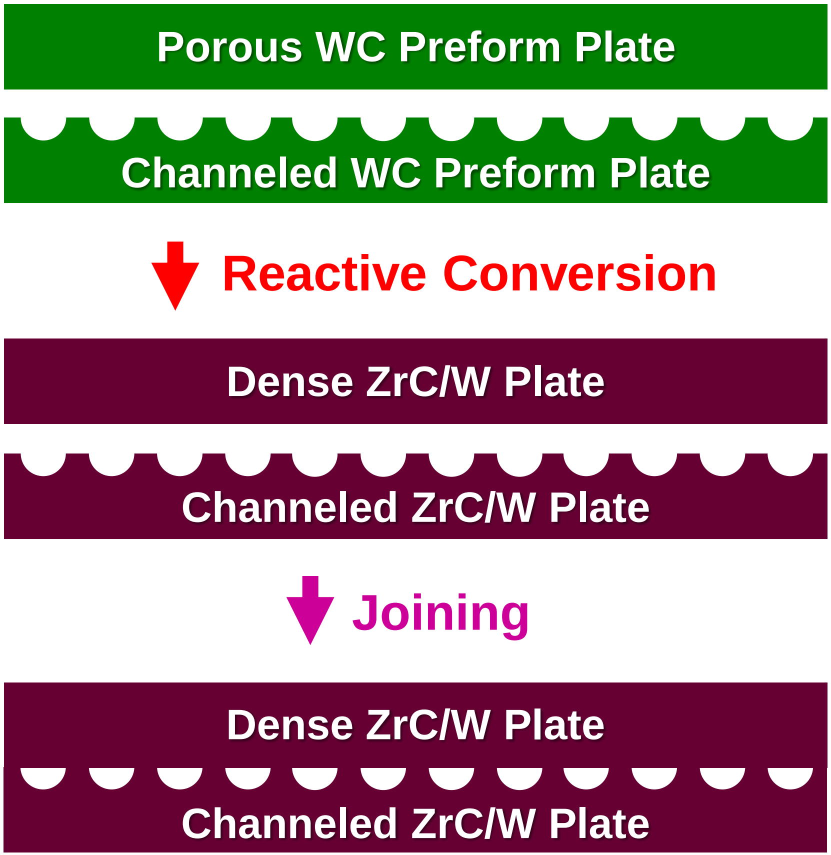
Component Joining



Fabricate pairs of porous WC preform plates (one with patterned channels)

Generate net-shape/size dense ZrC/W plates via patented DCP process

Diffusion bond pairs of ZrC/W plates; connect to headers and tubing

"Ceramic-metal composites for heat exchangers in concentrated solar power plants," M. Caccia, M. Tabandeh-Khorshid, G. Itskos, A. R. Strayer, A. S. Caldwell, S. Pidaparti, S. Singnisai, A. D. Rohskopf, A. M. Schroeder, D. Jarrahbashi, T. Kang, S. Sahoo, N. R. Kadasala, A. Marquez-Rossy, M. H. Anderson, E. Lara-Curzio, D. Ranjan, A. Henry, K. H. Sandhage*, *Nature*, 562 (7727) 406-409 (2018).

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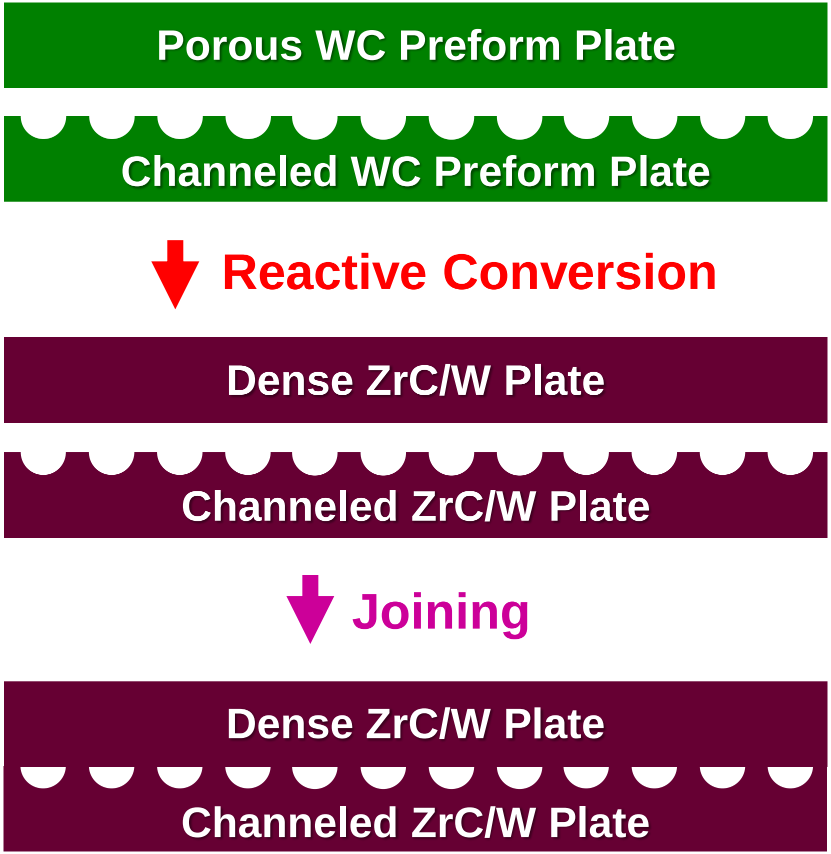
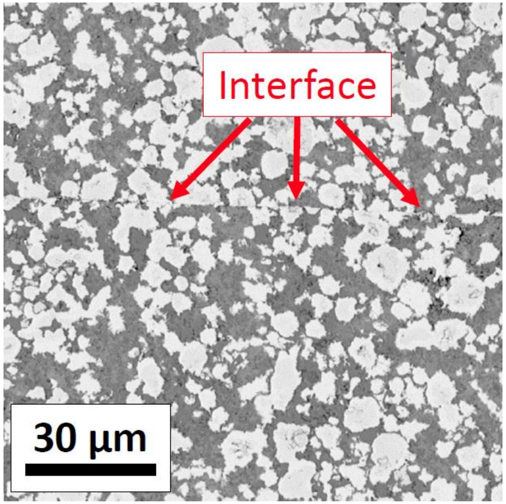
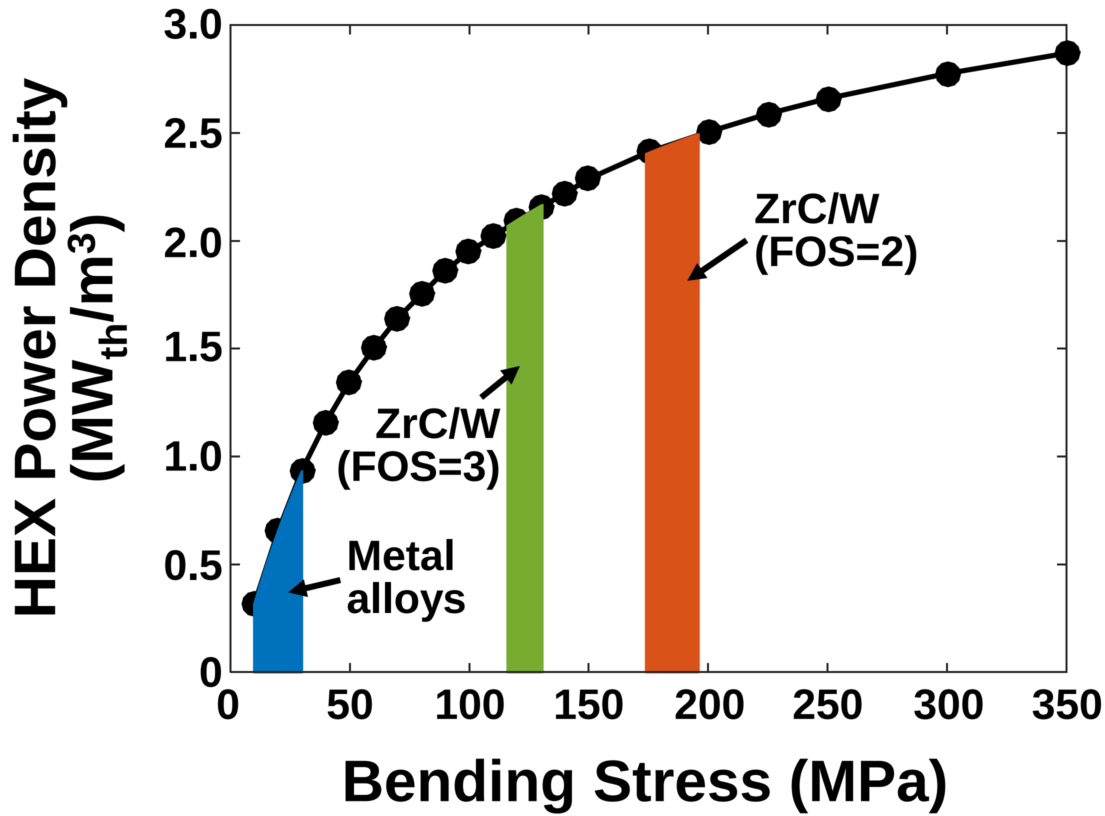


Fabricate pairs of porous WC preform plates (one with patterned channels)

Generate net-shape/size dense ZrC/W plates via patented DCP process



Heat Exchanger Performance Simulation



For a 17.5 MW_{th} HEX operating with 95% effectiveness for heat transfer from molten $MgCl_2$-KCl at 800°C to sCO_2 (400,000 channels, 2 mm dia., 2.5 m long)

(with Ranjan group, Georgia Tech)

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Shape-Preserving Chemical Transformation

- **Fluid/Solid Reactions (displacement, additive, subtractive)**
  - Macroscale/microstructured inorganic templates (liquid/solid reactions)
  - Microscale/nanostructured inorganic templates (gas/solid reactions)
- **Conformal Coating (inorganic, organic templates)**
  - Surface sol-gel-based oxide deposition
  - Protein-enabled oxide and oxide/organic deposition
  - Electroless metal deposition

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Diatoms (micro-algae)

- Diatoms (*Bacillariophyceae*) are single-celled photosynthetic eukaryotes (algae) found in abundance in a wide variety of aquatic environments (e.g., arctic and equatorial; marine and freshwater).
- Most populous of the microalgae in the oceans: responsible for 40% of eukaryotic phytoplankton production and 25% of primary biomass production.
- Diatoms form rigid cell walls (frustules) of specialized organic macromolecules and amorphous, partially-hydrated silica (SiO_2).

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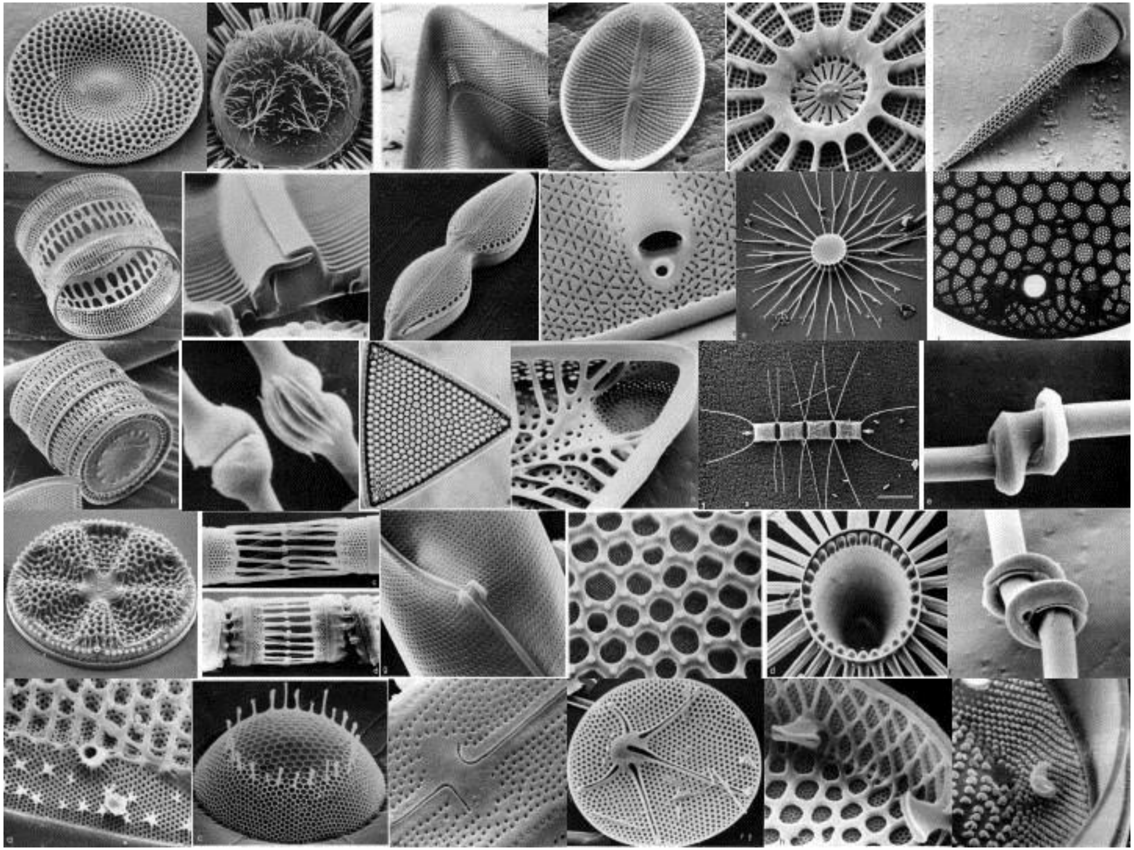
Diatoms: 3-D Micro/Nanoscale SiO_2 Assembly



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. Patent No. 7,067,104;*
U.S. Patent No. 7,204,971;
U.S. Patent No. 7,615,206)**

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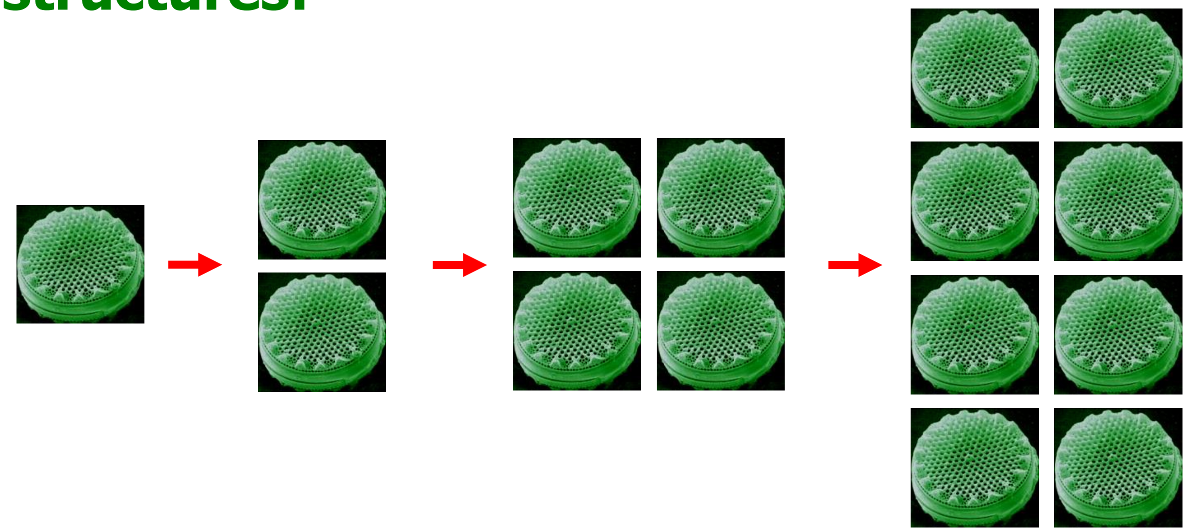
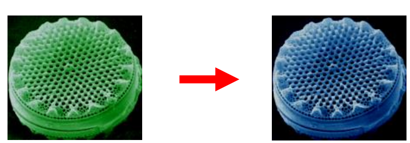
Biological Assembly and Shape-preserving Inorganic Conversion (BASIC)

- **Use microorganisms as biofactories to precisely and rapidly generate enormous numbers (2^n) of rigid, 3-D microscale structures:**



- **Use synthetic methods to alter the chemistry, but not the shape, for desired properties.**



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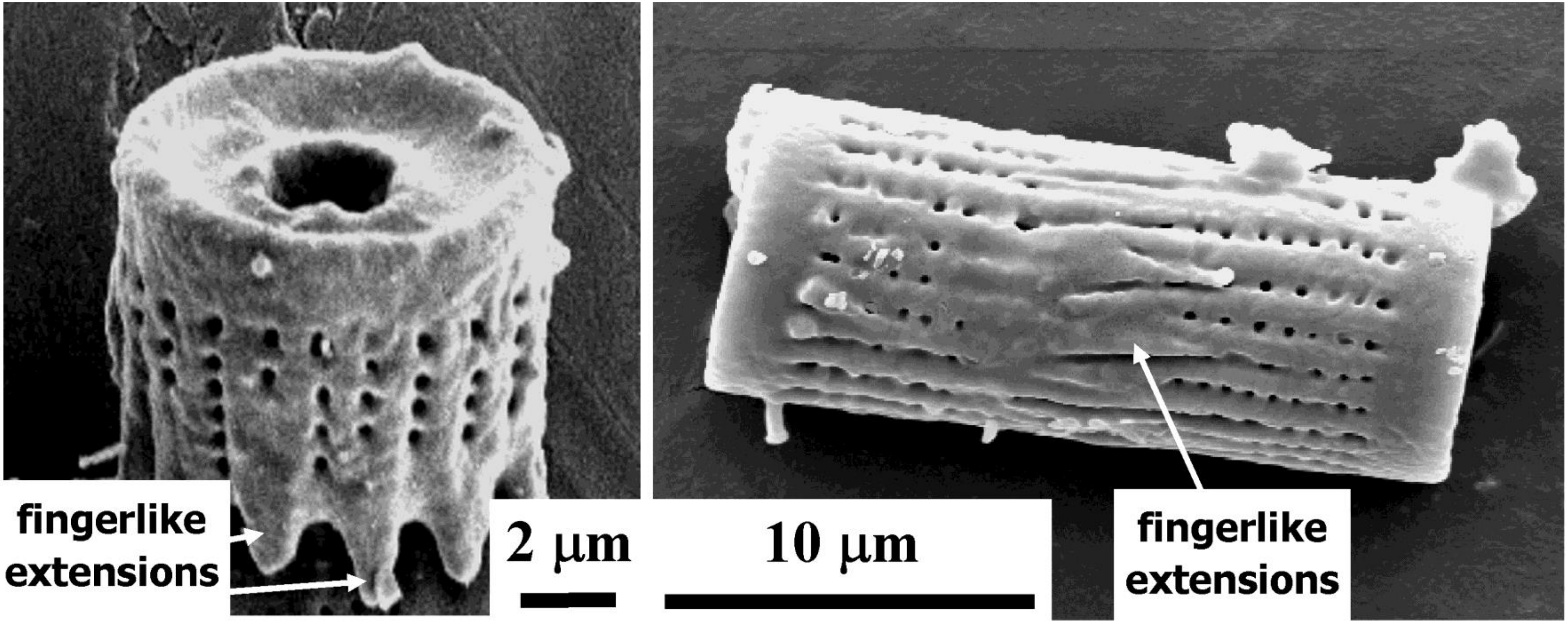
Aulacoseira Diatom Frustules



Secondary electron images

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

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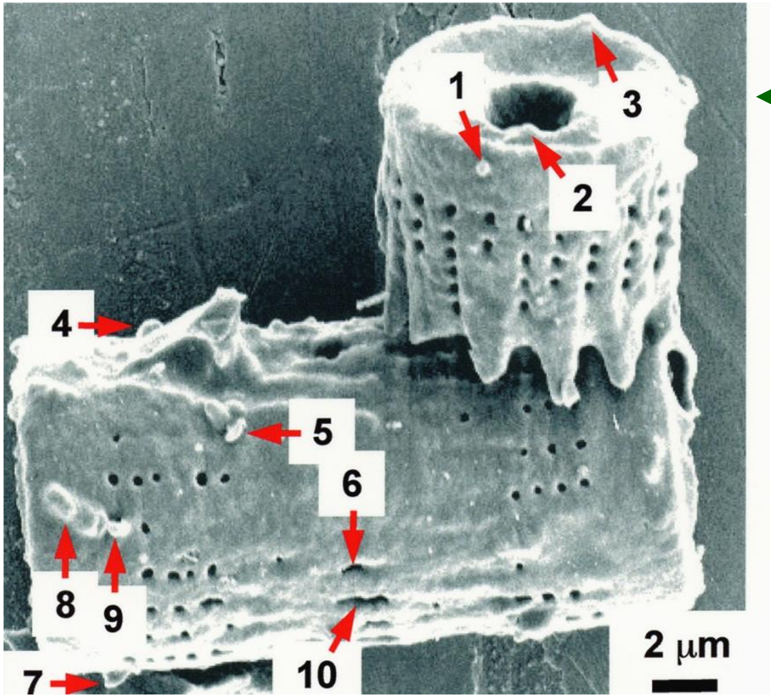
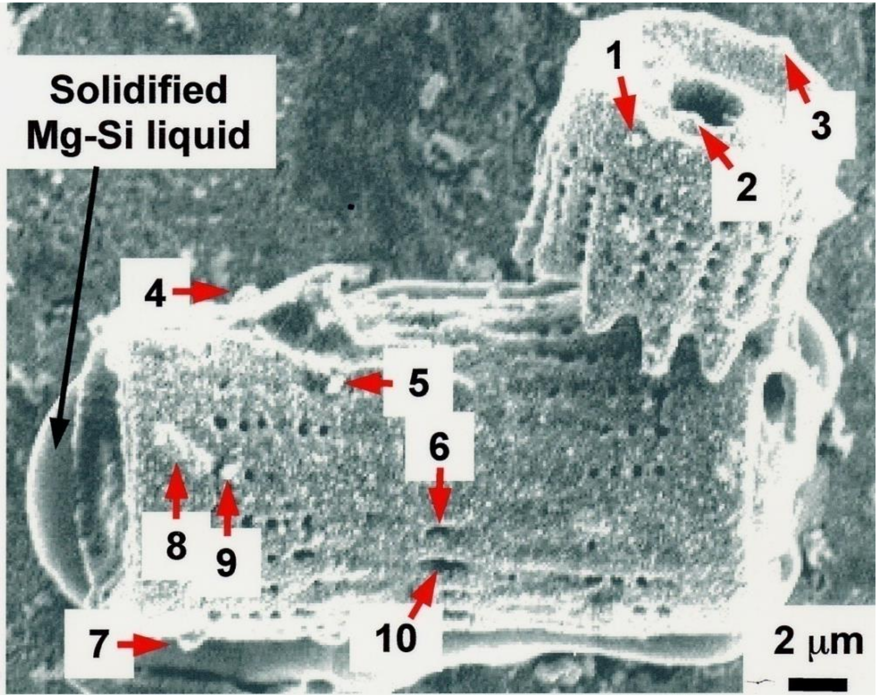
MgO Replicas (900°C, 4 h)



$\leftarrow$ SiO_2 frustules

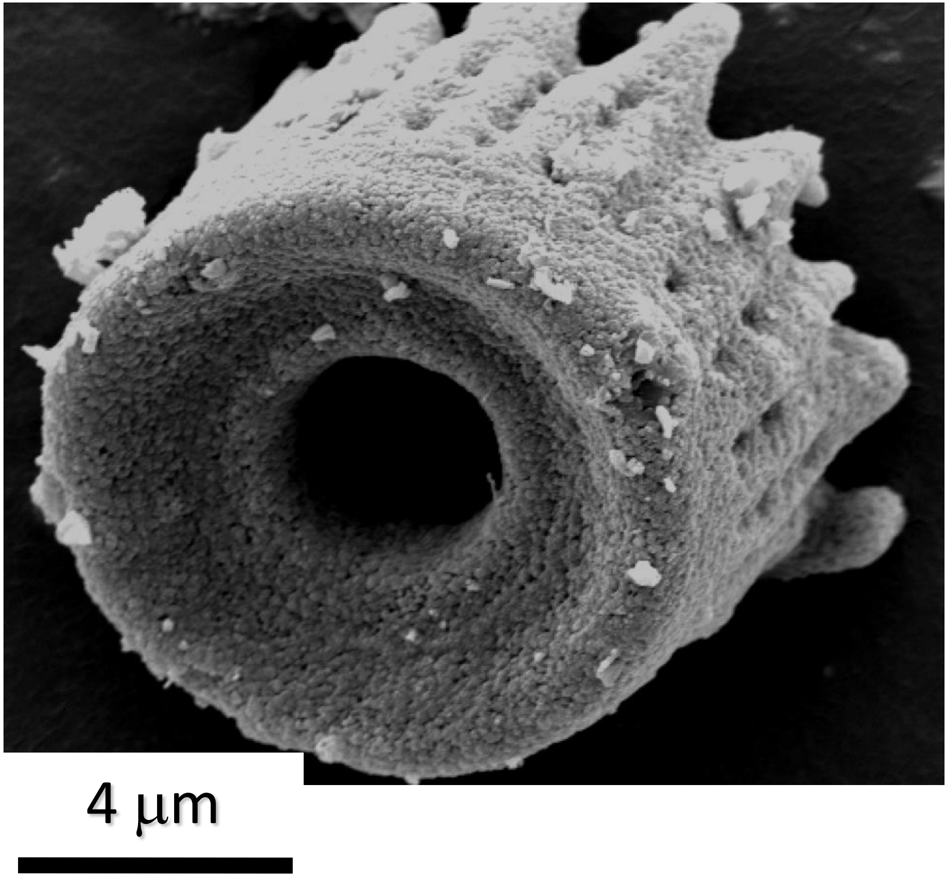
MgO capsules



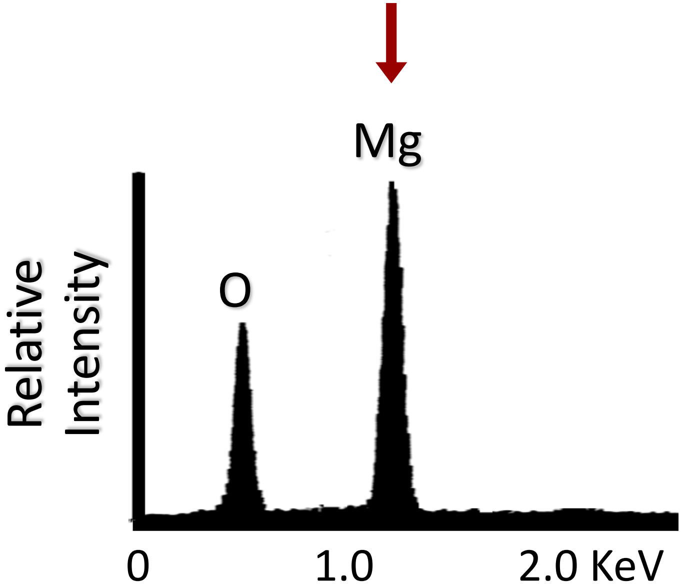
$$2Mg(g) + SiO_2(s)$$
$$\Rightarrow 2MgO(s) + \{Si\}$$

K. H. Sandhage, et al., *Adv. Mater.*, 14, 429 (2002).

MgO Replicas (900°C, 4 h)

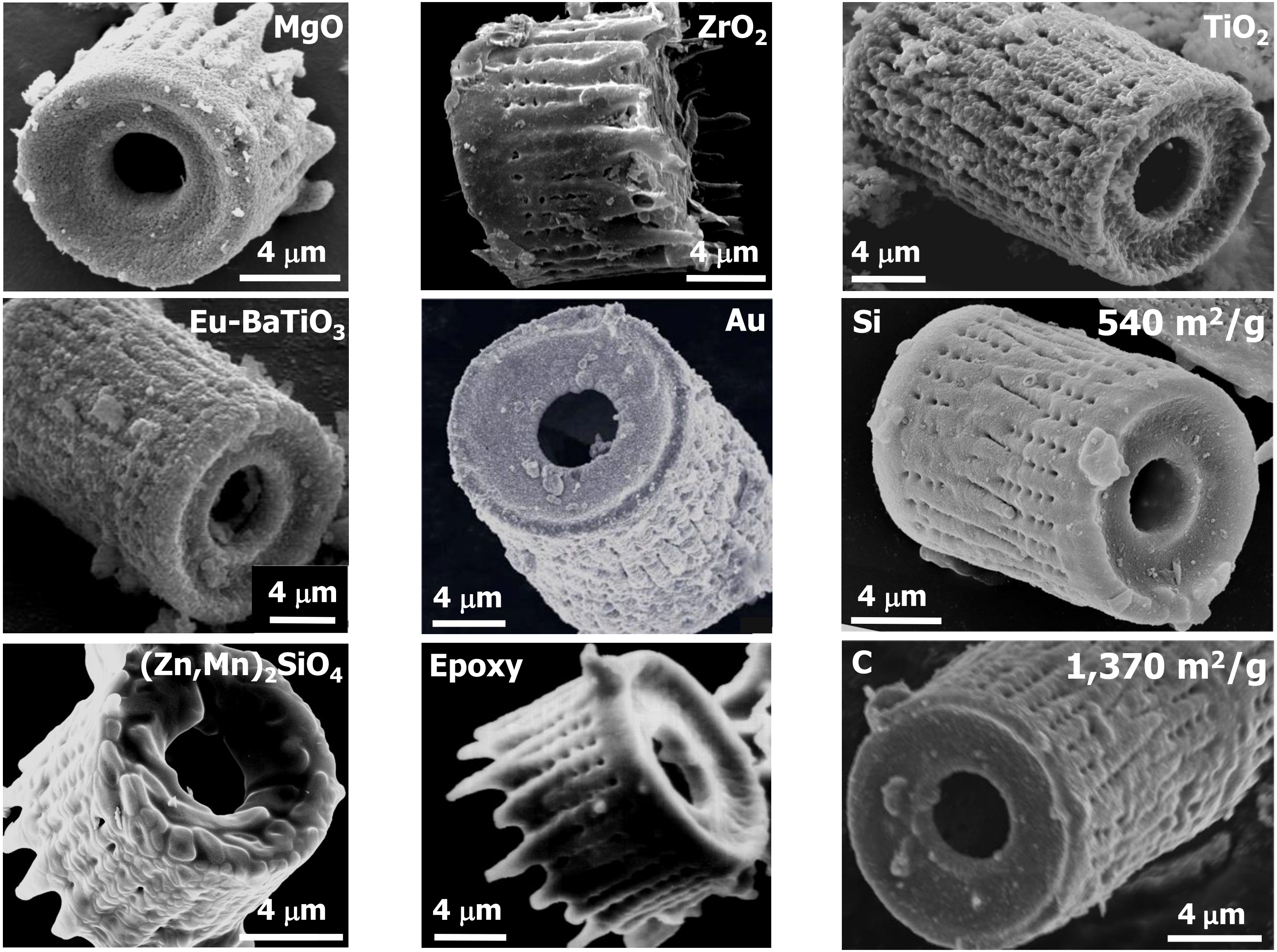


Energy-dispersive x-ray analysis

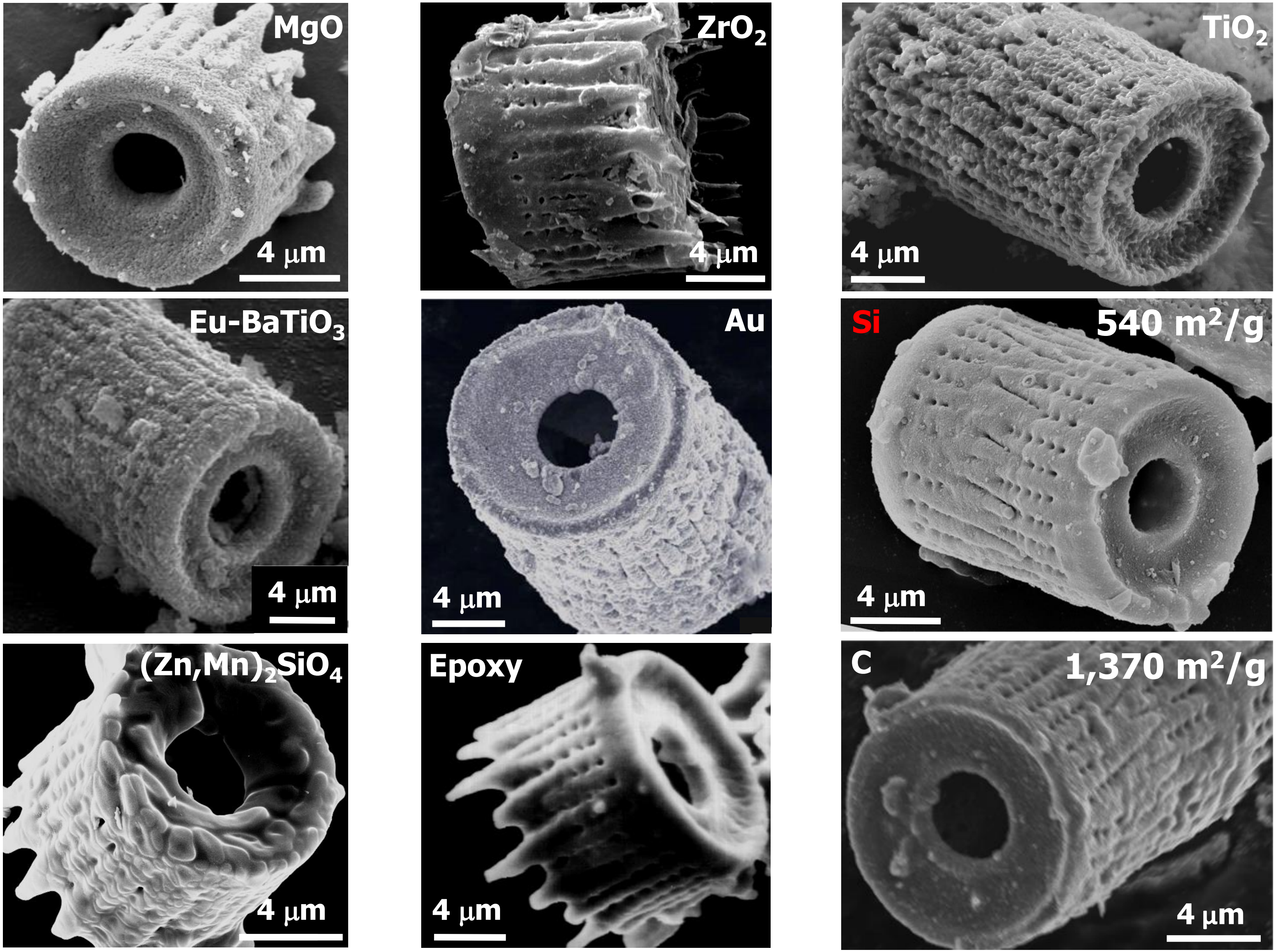


K. H. Sandhage, et al., *Adv. Mater.*, 14, 429 (2002).

Diatom Alchemy



Diatom Alchemy



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).**

- **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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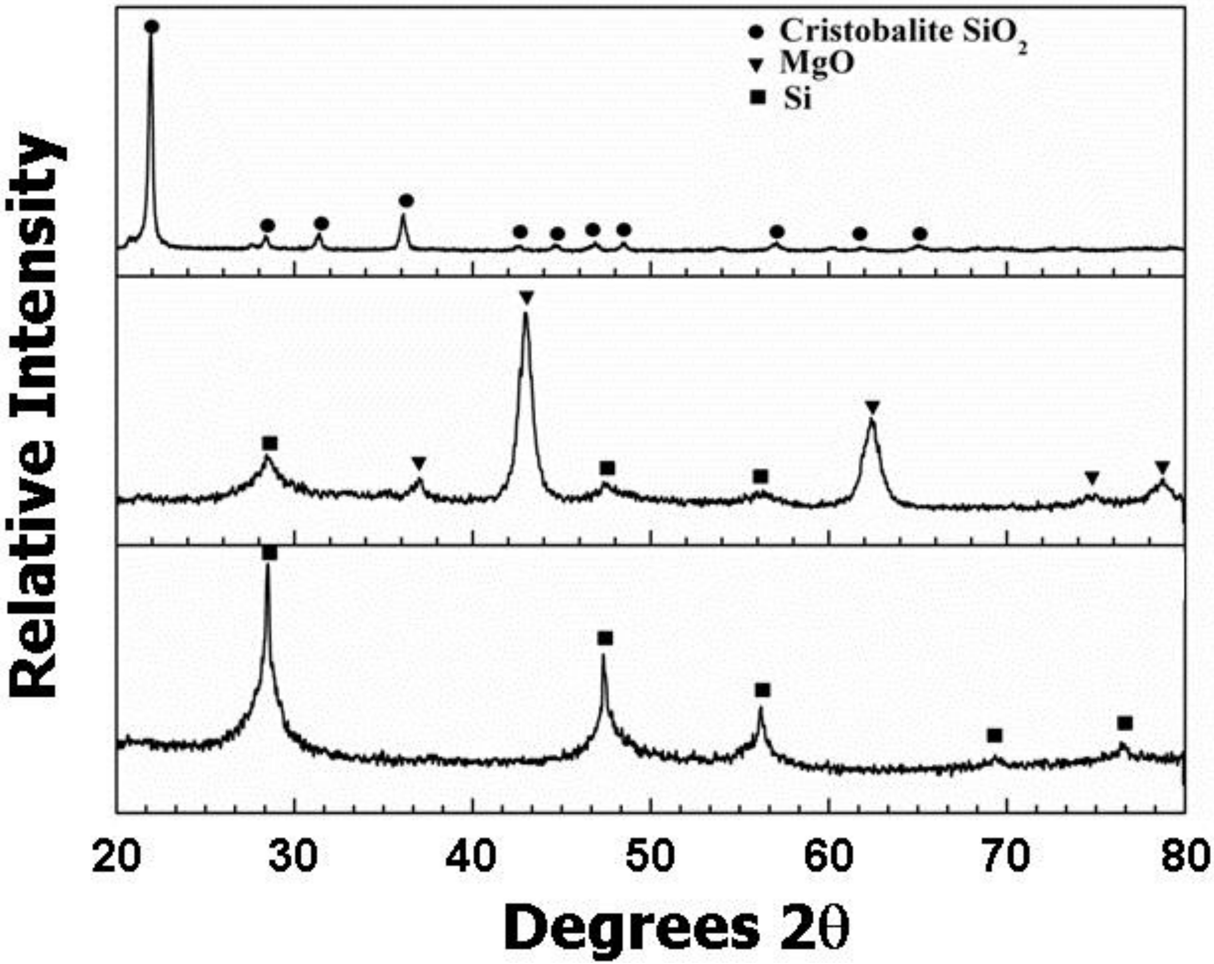
Conversion into Si-based Replicas



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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Magnesiothermic Reduction of SiO_2 -> Si

- **For the reaction:**

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

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

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

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

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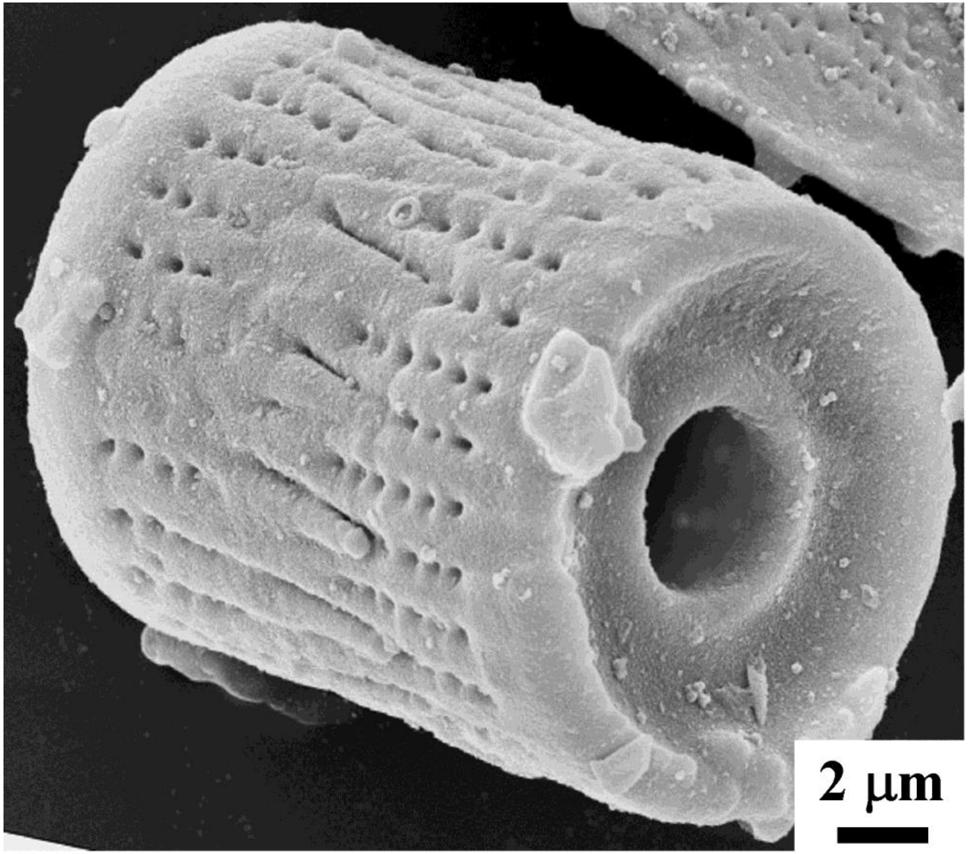
Conversion into Si Replicas



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

Secondary electron image

Surface Area: 541 m^2/g (BET analysis)

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

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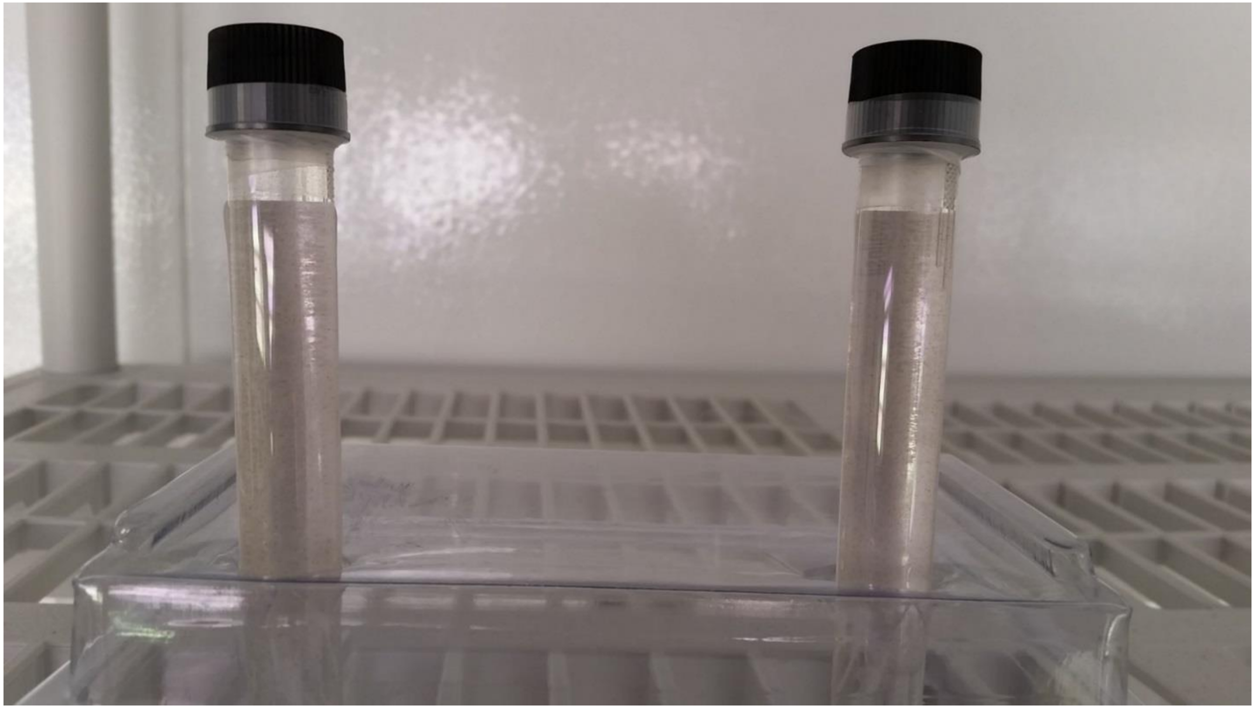
Culturing of Coscinodiscus wailesii diatoms



(Diatom cultures obtained from the Provasoli-Guillard National Center for the Culture of Marine Phyto-plankton, CCMP, Bigelow Laboratory for Ocean Sciences, West Boothbay Harbor, Maine)

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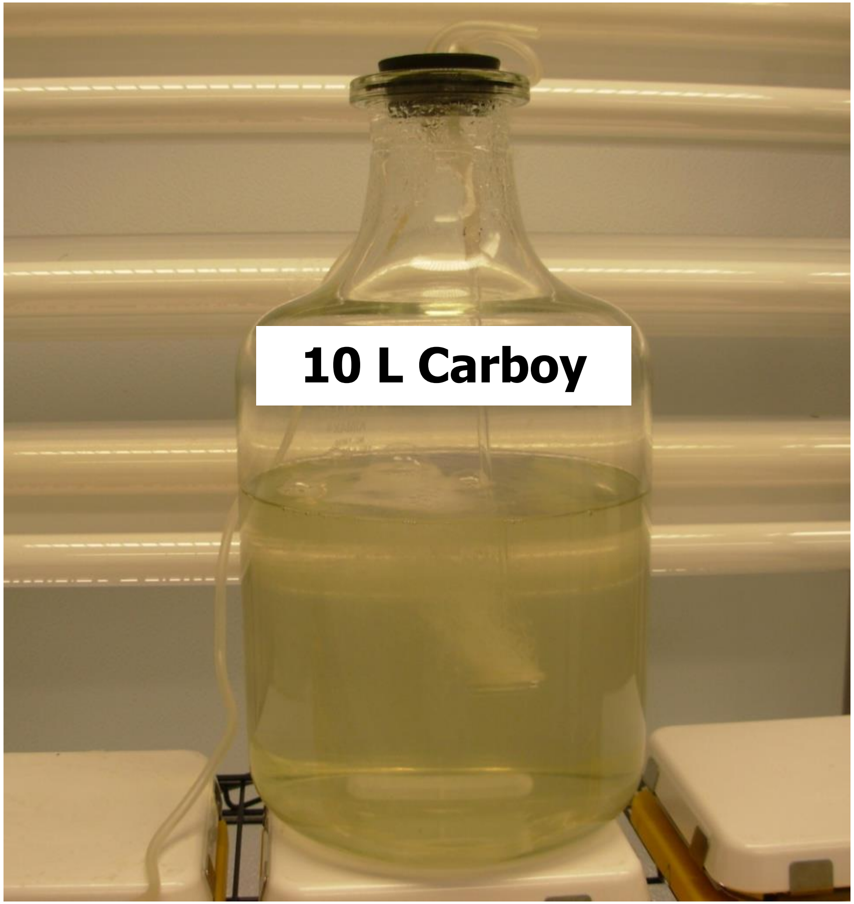
Culturing of Coscinodiscus wailesii diatoms



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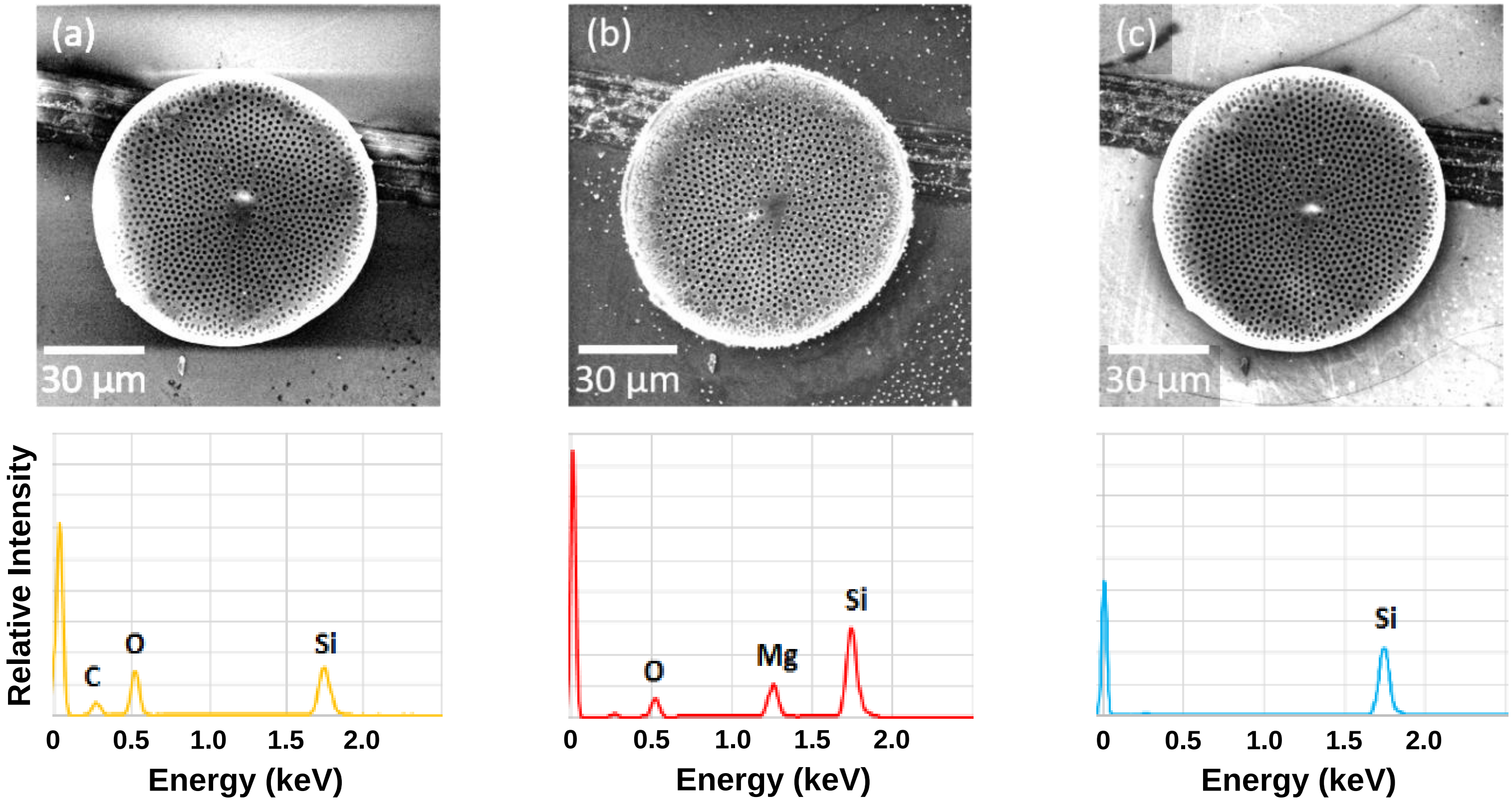
Conversion of C. wailesii frustule into Si



SiO_2 **MgO/Si** **Porous Si**

SE images, EDX analyses at various stages of conversion of a *C. wailesii* frustule into Si

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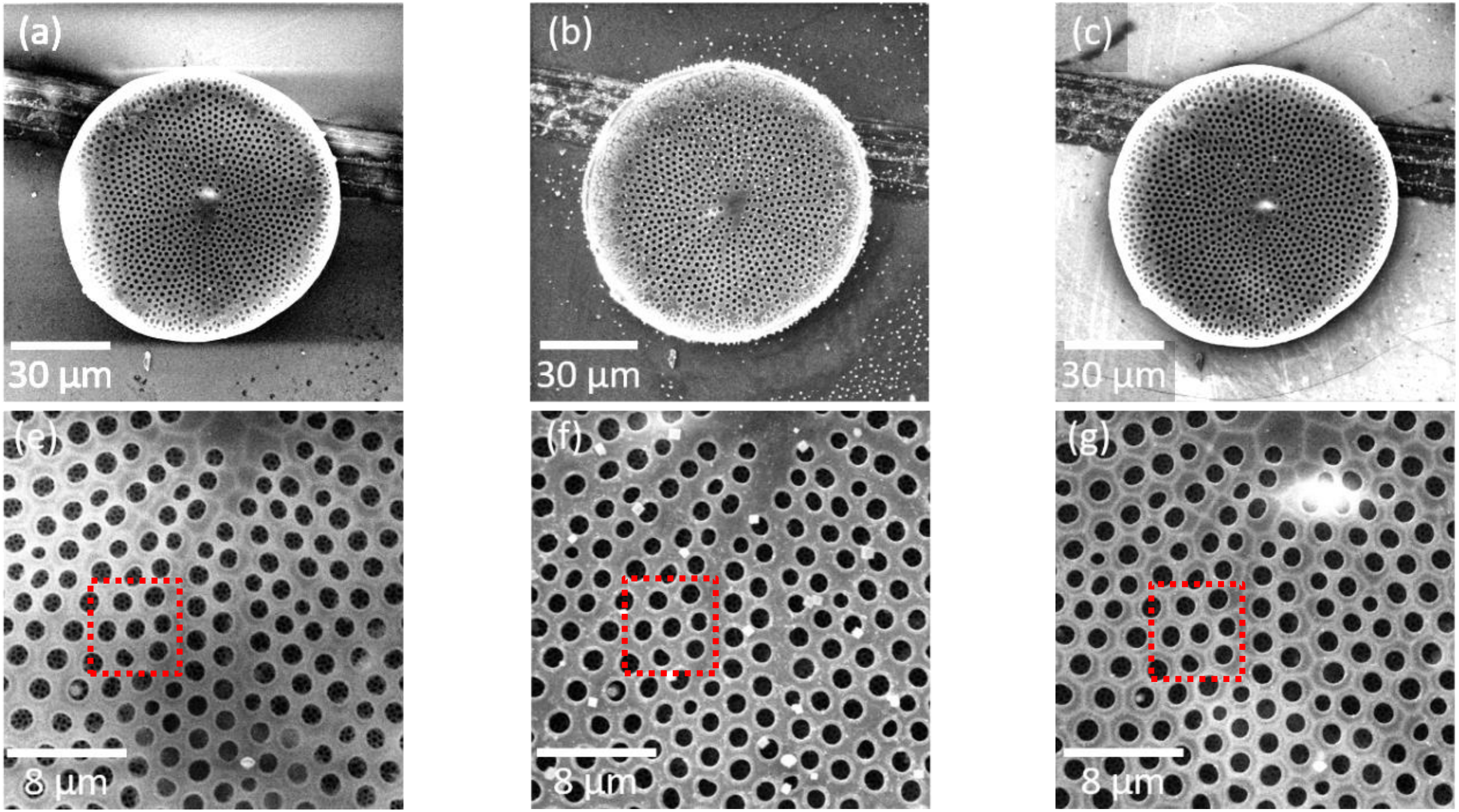
Conversion of C. wailesii frustule into Si



SiO_2 MgO/Si Porous Si

SE images of the same *C. wailesii* frustule at various stages of conversion into Si

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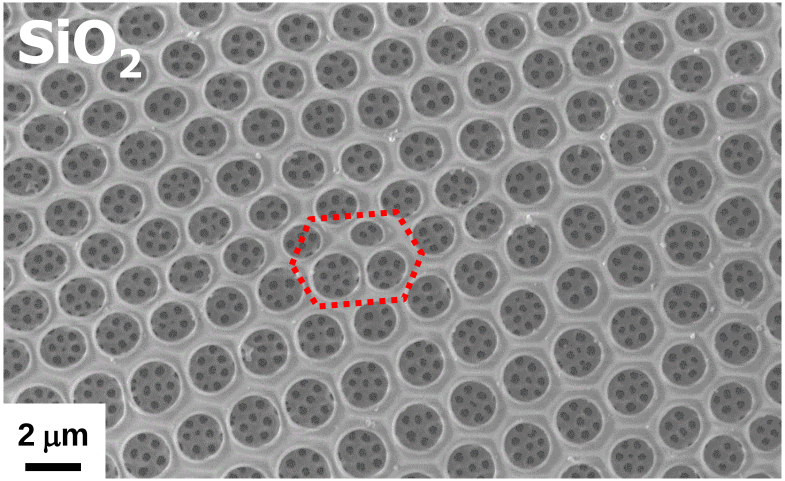
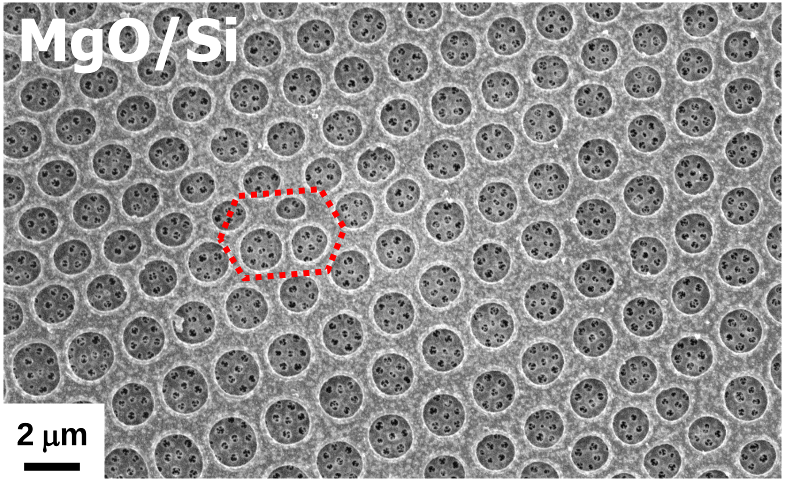
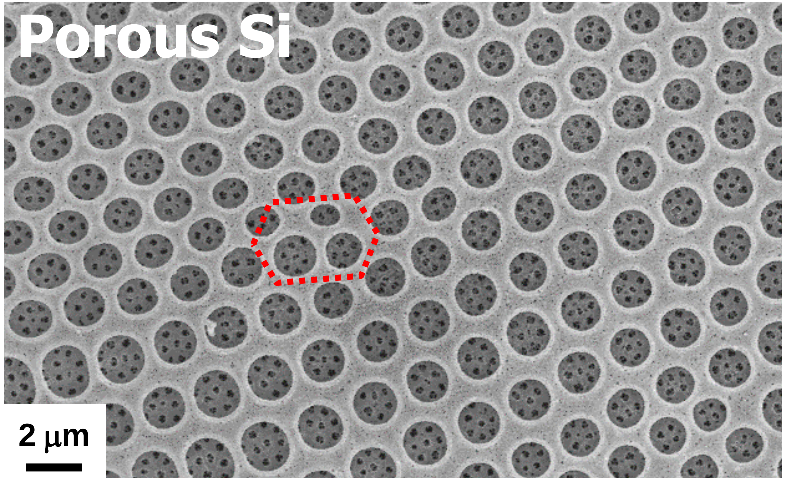
Conversion of *C. wailesii* frustule into Si







SE images of the same *C. wailesii* frustule at various stages of conversion into Si

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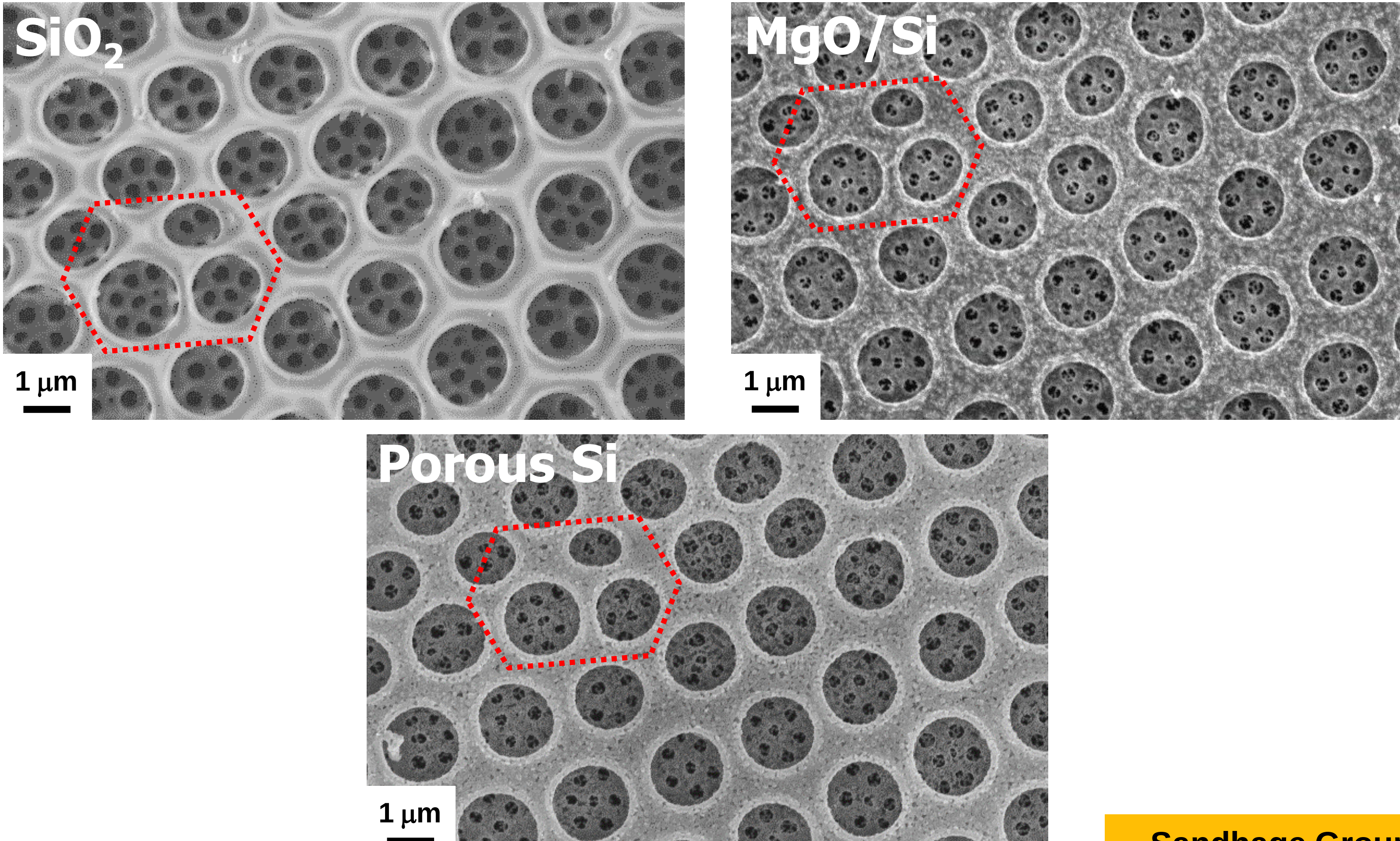
Conversion of C. wailesii frustule into Si



SE images of the same *C. wailesii* frustule at various stages of conversion into Si

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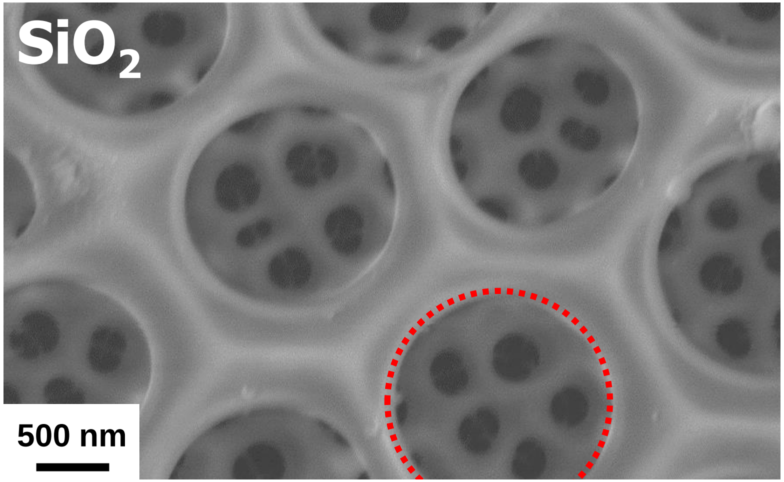
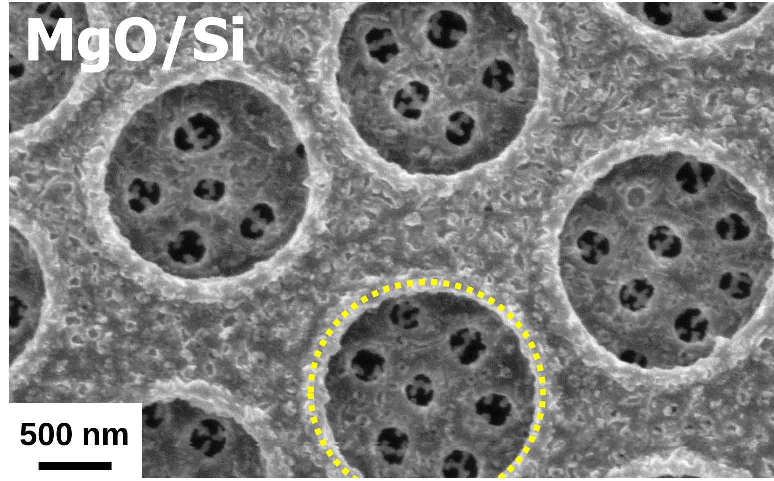
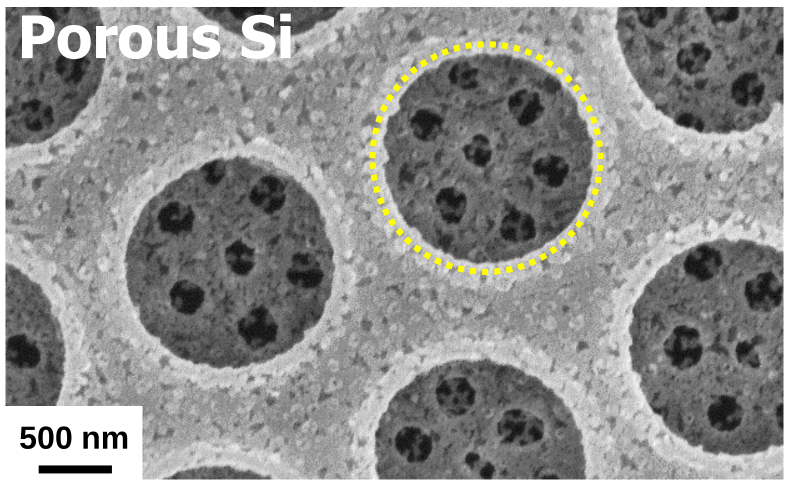
Conversion of C. wailesii frustule into Si







SE images of the same *C. wailesii* frustule at various stages of conversion into Si

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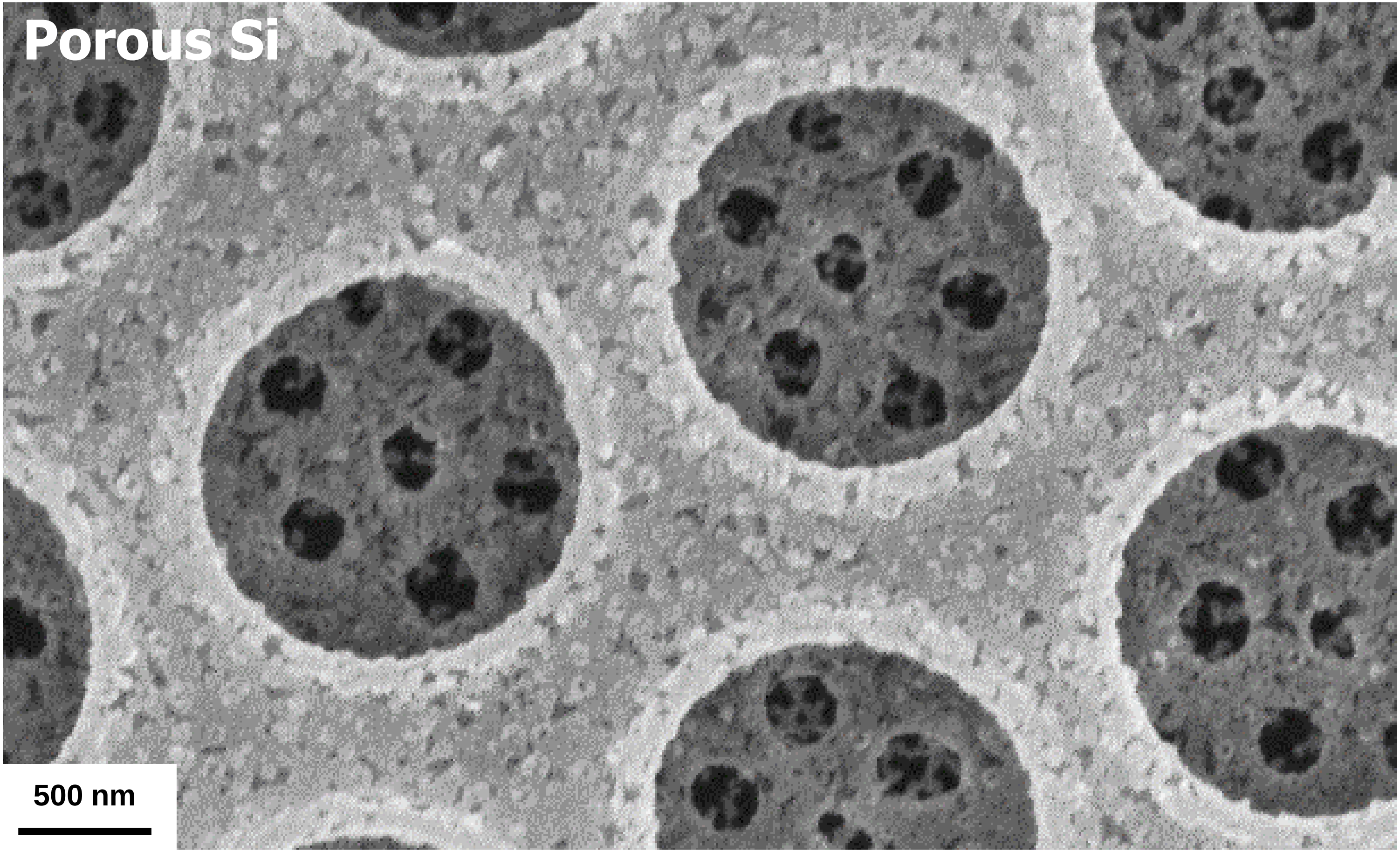
Conversion of *C. wailesii* frustule into Si



SE image of the foramen layer of a Si replica of a *Coscinodiscus wailesii* valve

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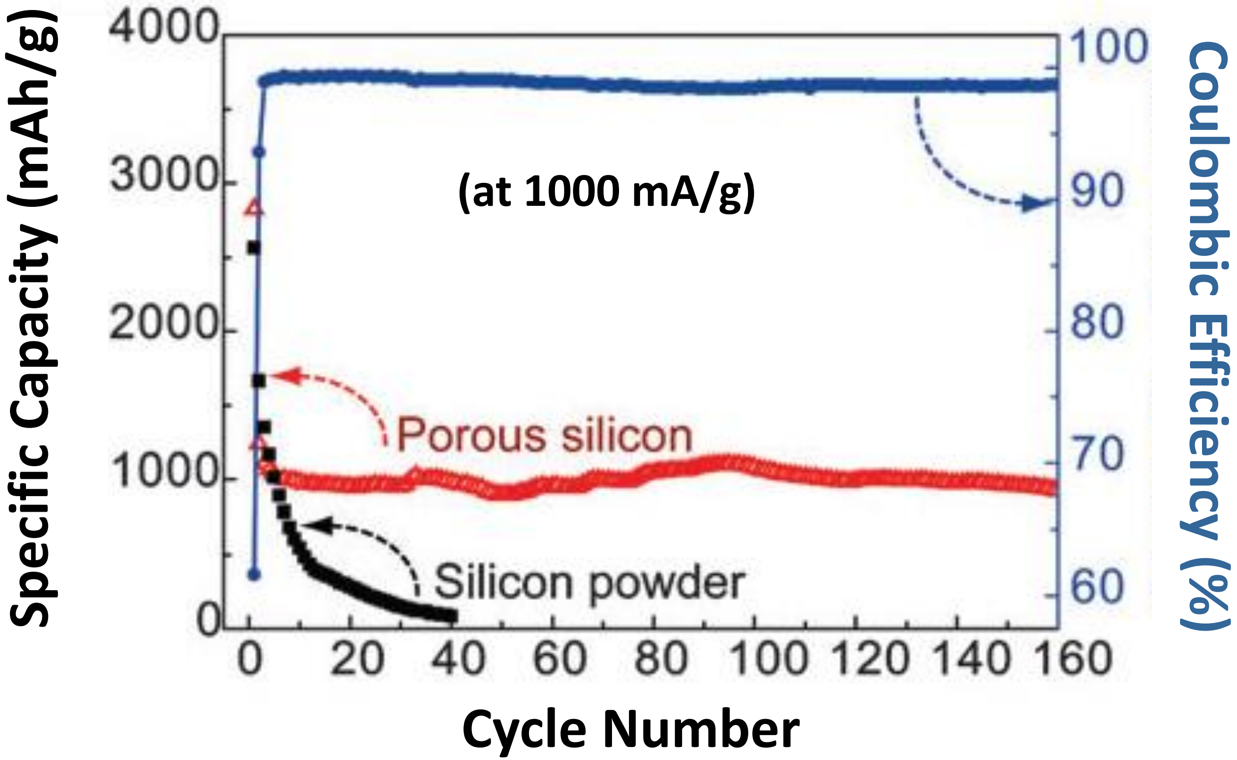
Some Applications for Porous Si Replicas

◆ Porous silicon anodes for lithium ion batteries

- K. H. Sandhage, Z. Bao, *U.S. Patent #7,615,206*, Nov. 10, 2009.
- Y. Yu, et al., *Adv. Mater.*, 22, 2247 (2010).
- A. Xing, et al., *Chem. Commun.*, 49 (60) 6743 (2013).
- F. H. Du, et al., *Adv. Mater.*, 26, 6145 (2014).
- J. Liu, et al., *Angew. Chemie Int. Edn.*, 54, 9632 (2015).
- W. C. Cho, et al., *Nano Lett.*, 16, 7261 (2016).
- B. Li, et al., *Small*, 12, 5281 (2016).
- X. Zuo, et al., *ACS Nano*, 11, 889 (2017).
- S. Gui, et al., *ACS Appl Mater. Interf.*, 9, 420894 (2017).
- B. Kim, et al., *J. Mater. Chem. A*, 6, 3028 (2018).
- M. Choi, J.-C. Kim, D.-W Kim, *Sci. Reports*, 8, 960 (2018).

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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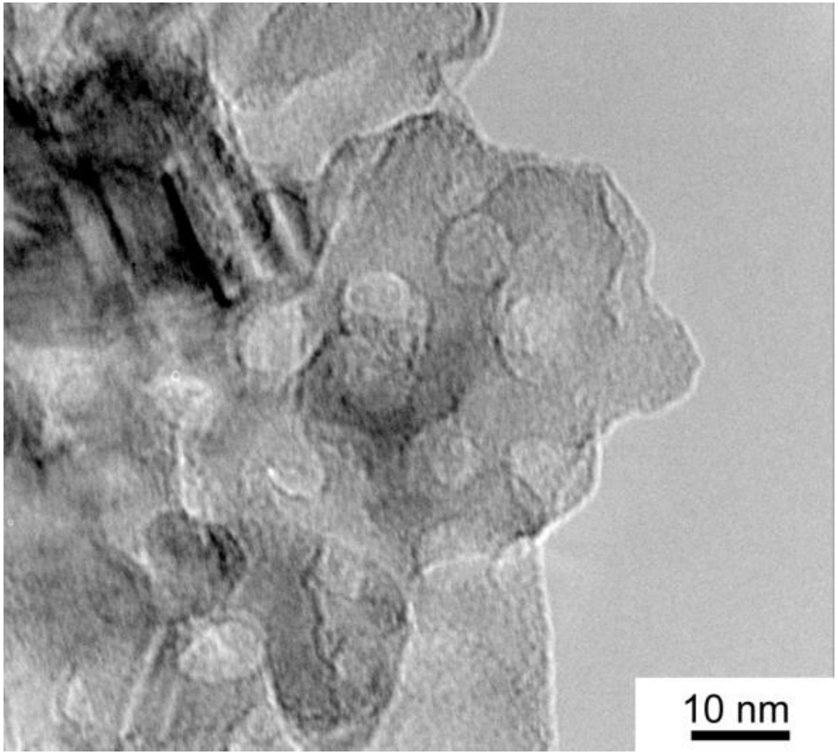
Porous Si for Lithium Ion Battery Anodes



Transmission Electron Image

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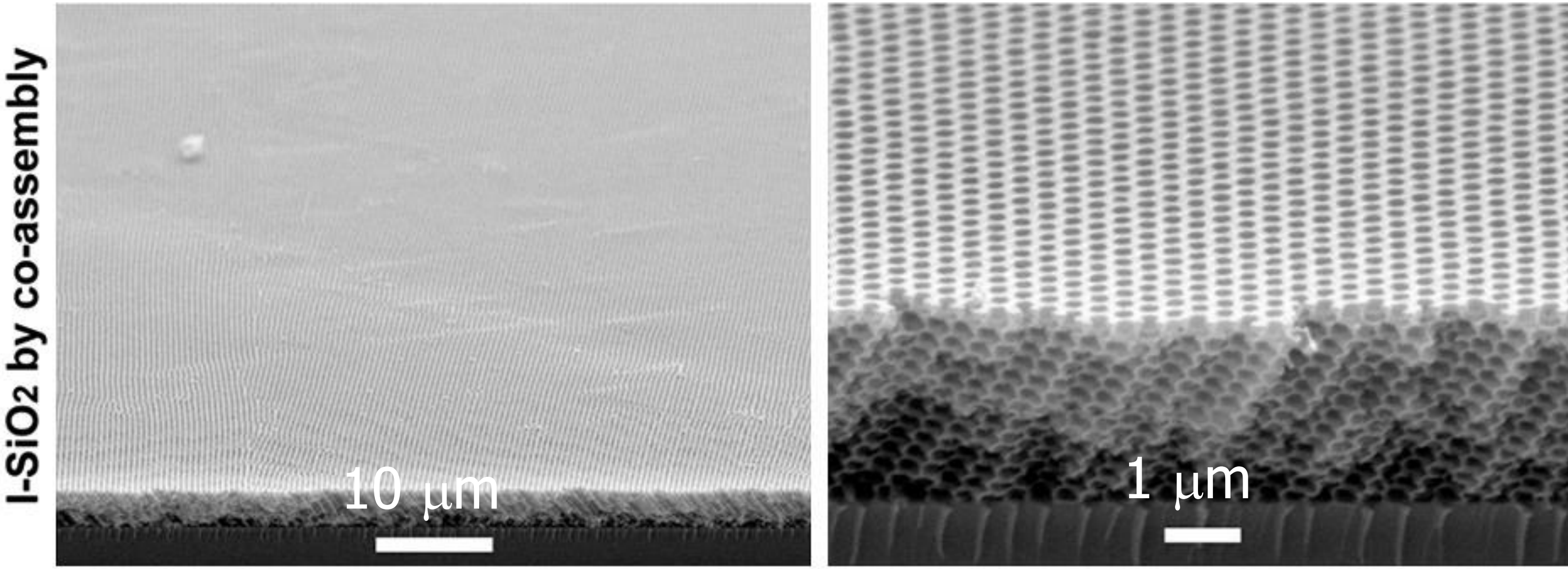
◆ Inverse Opals

- B. Hatton, et al., *PNAS*, 107, 10354 (2010).
- F. Gallego-Gomez, et al., *Adv. Mater.*, 23 (44) 5219 (2011).
- Z. Jiang, et al., *Current Nanosci.*, 12, 482 (2016).

Synthetic Templates for Gas/Solid Displacement Reactions

Large area, low defect density, SiO_2 Inverse Opals



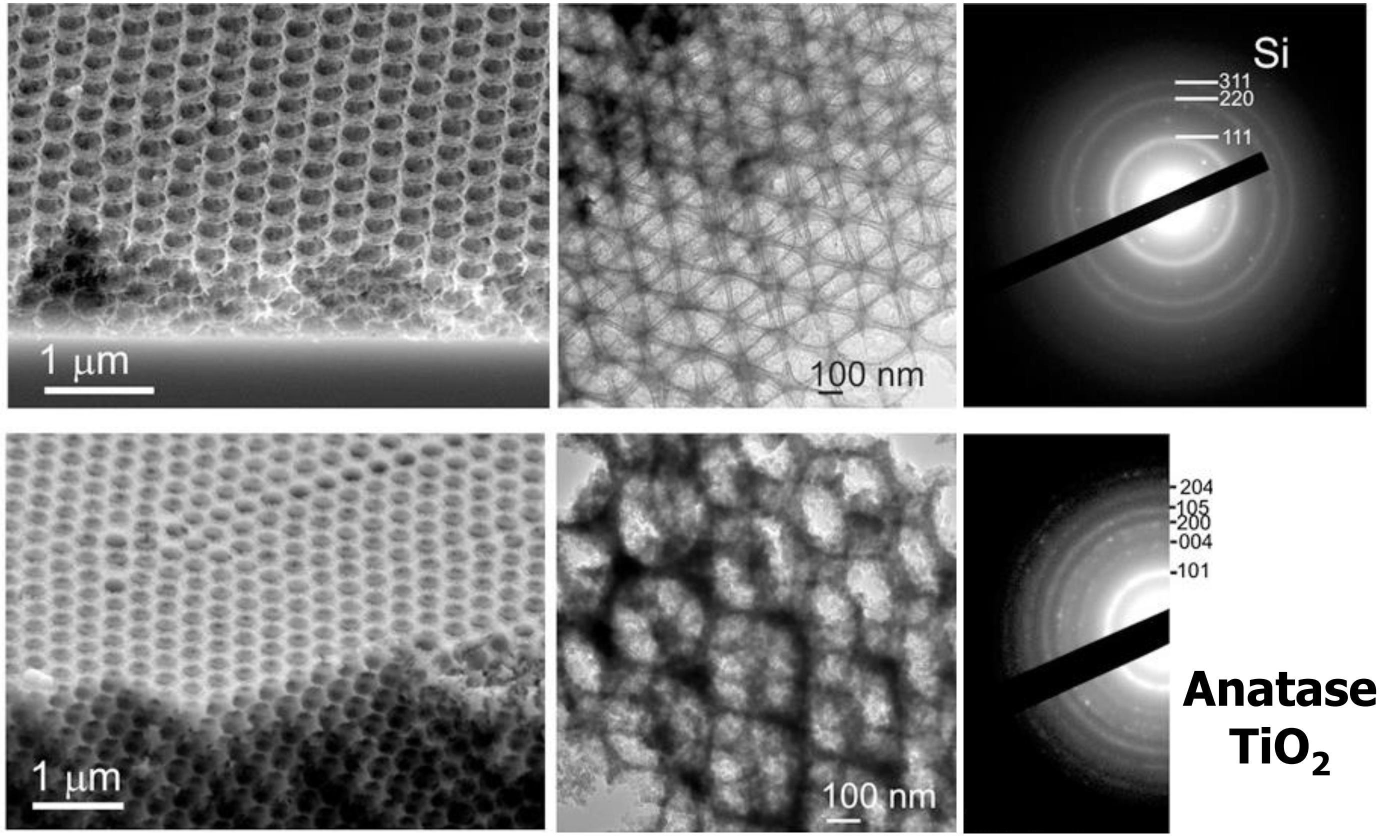
(After evaporative co-deposition of TEOS/PMMA nanospheres, then firing at 500°C for 5 h in air)

(B. Hatton, L. Mishchenko, J. Aizenberg)

Morphology-preserving Reactive Conversion

Si Inverse Opal

TiO_2 Inverse Opal



SE images **TE Images** **SAED Patterns**

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- Z. Jiang, et al., *Current Nanosci.*, 12, 482 (2016).

◆ Photoluminescent particles

- Z. Bao, et al., *Nature*, 446, 172 (2007).
- S. Maher, et al., *Adv. Funct. Mater.*, 25, 5107 (2015).

◆ High-sensitivity sensors

- Z. Bao, et al., *Nature*, 446, 172 (2007).
- Z. Xia, et al., *Adv. Opt. Mater.*, 2, 235-239 (2014).

Some Applications for Porous Si Replicas

- **Porous, photothermal particles for therapeutics**
  - X. Yu, et al., *Biomater.,* 143, 120 (2007).
  - M. Guo, et al., *Micropor. Mesopor. Mater.,* 142, 194 (2011).
  - S. Maher, et al., *Adv. Healthcare Mater.*, 5, 2667 (2016).
- **Supercapacitors**
  - Q. J. Le, et al., *J. Mater. Chem.,* 5, 10856 (2017).
- **Solar cells**
  - S. Arunmetha, et al., *J. Electron. Mater.,* 47, 493 (2017).
  - S. Venkateswaran, et al., *Phosph., Sulfur, Silicon, Rel. Elements*, 188, 1178 (2013).
- **Catalytic/photocatalytic particles**
  - F. Dai, et al., *Nature Commun.,* 5, 3605 (2014).
  - S.-T. Liu, et al., *Dalton Trans.*, 45, 2369 (2016).
  - P. Gao, et al., *Chem. Commun.,* 53, 3114 (2018).
- **Thermoelectrics**
  - J. Szczech, et al., *J. Solid State Chem.*, 181, 1565 (2008)
  - M. L. Snedaker, et al., *Chem. Mater*, 25, 4867 (2013).
  - K. Kikuchi, et al., Nanoscale Res. Lett., 12, 343 (2017).

=> **From 1 citation on Si via magnesiothermic reduction in 2007 (Z. Bao, et al., *Nature,* 446, 172 (2007))**

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- **Porous, photothermal particles for therapeutics**
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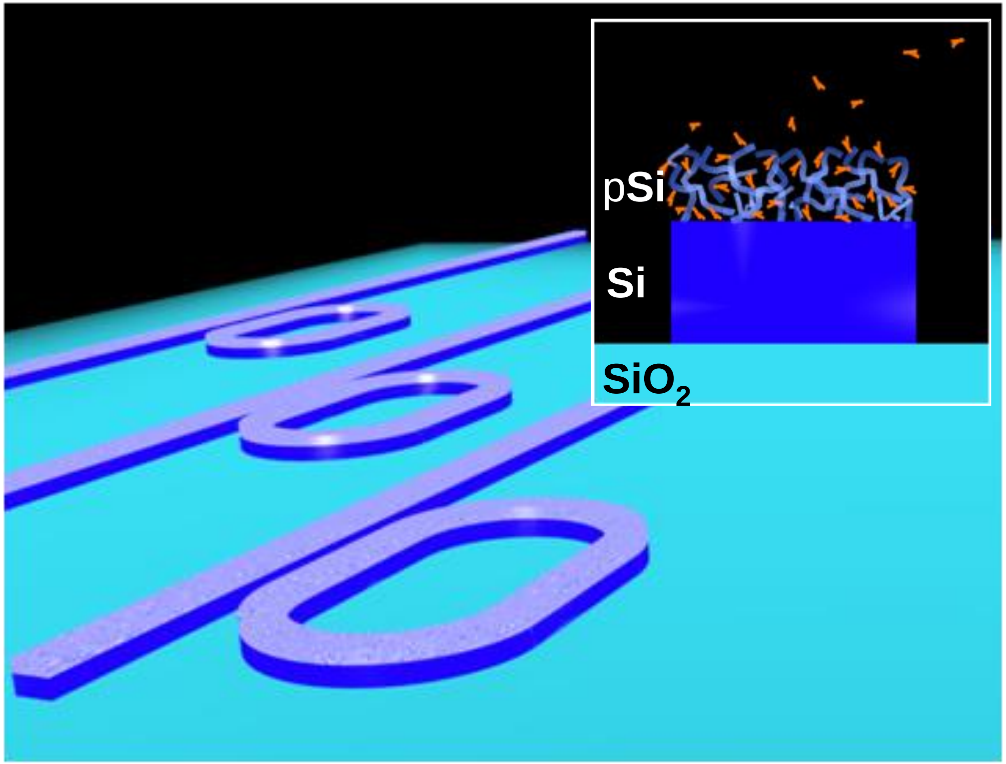
  - K. Kikuchi, et al., Nanoscale Res. Lett., 12, 343 (2017).

=> **From 1 citation on Si via magnesiothermic reduction in 2007 to over 4,800 citations to date**

Porous Si on μpatterned Silicon-on-Insulator (SOI) for Sensitive Optical Detection



"Racetrack" Resonator

(with Adibi group, Georgia Tech)

Sandhage Group
PURDUE
UNIVERSITY

Magnesiothermic Rxn-then-Pattern Process

SOI Wafer

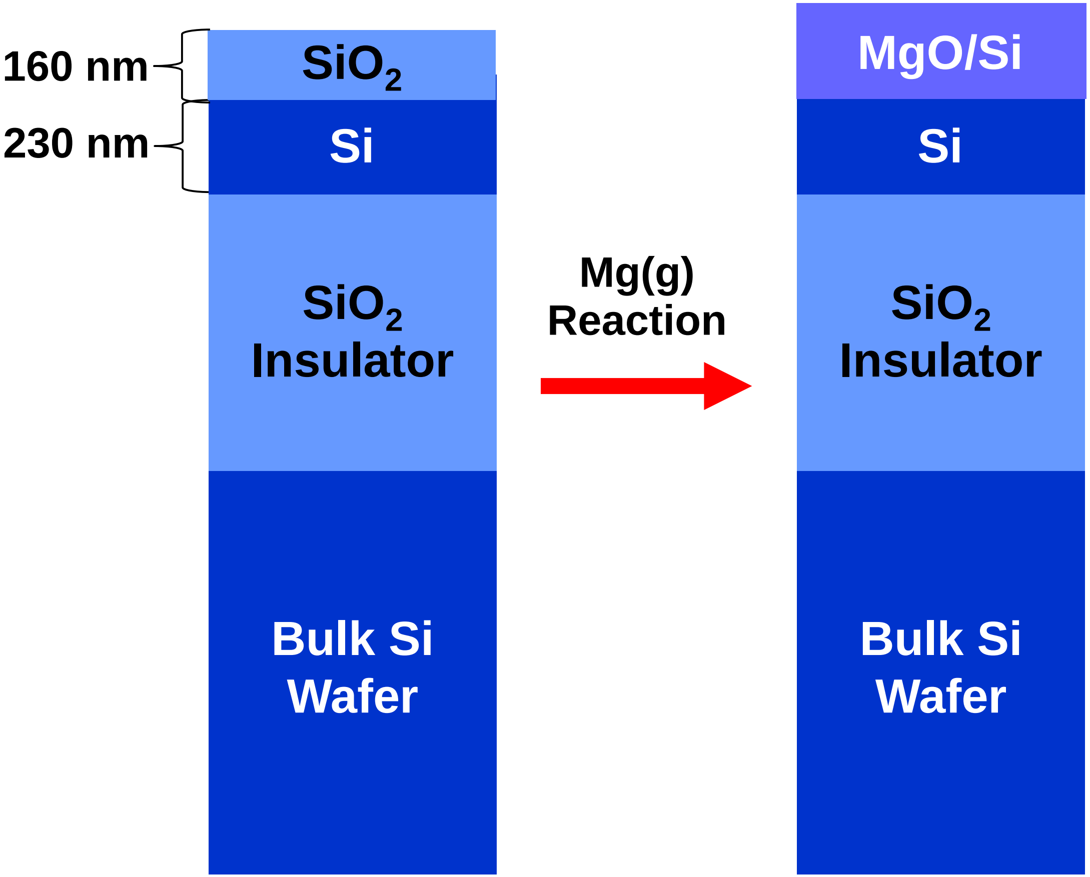
Sandhage Group

PURDUE UNIVERSITY

Magnesiothermic Rxn-then-Pattern Process

Oxidized SOI Wafer

Magnesiothermic Rxn-then-Pattern Process



Oxidized SOI Wafer

Sandhage Group

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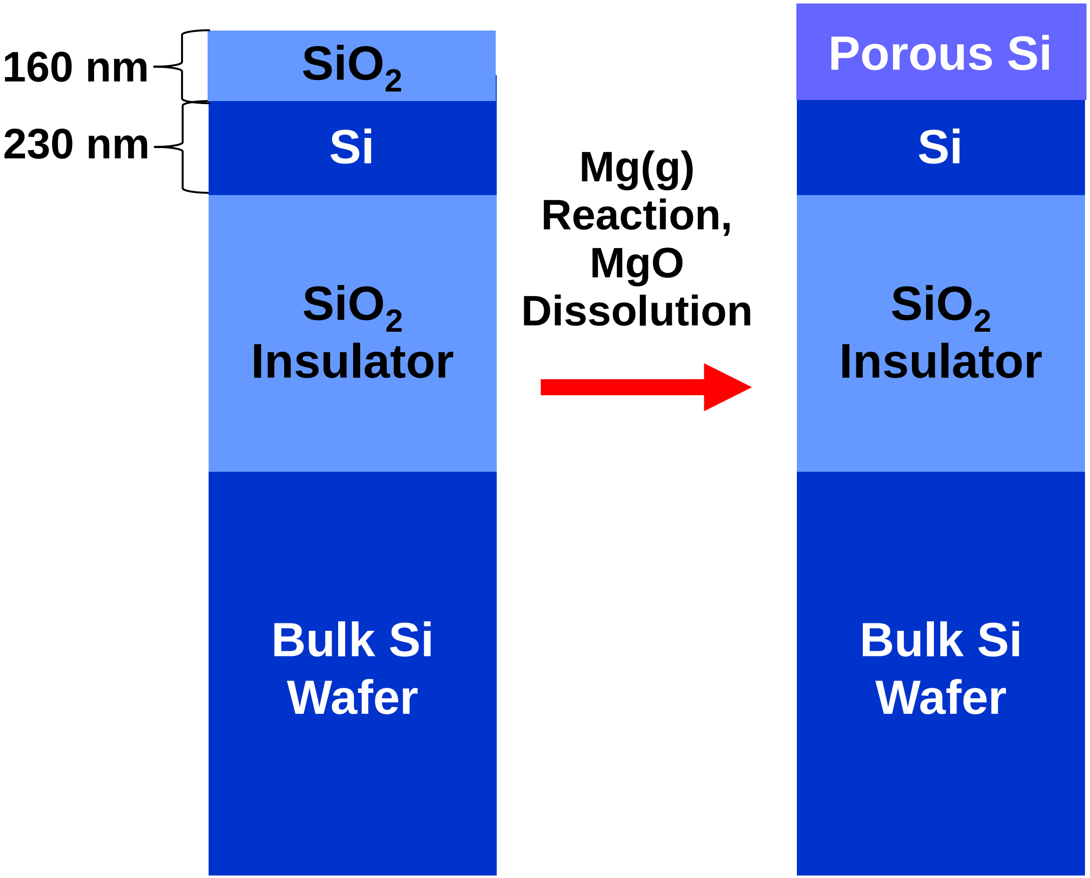
Magnesiothermic Rxn-then-Pattern Process



Oxidized SOI Wafer

Sandhage Group

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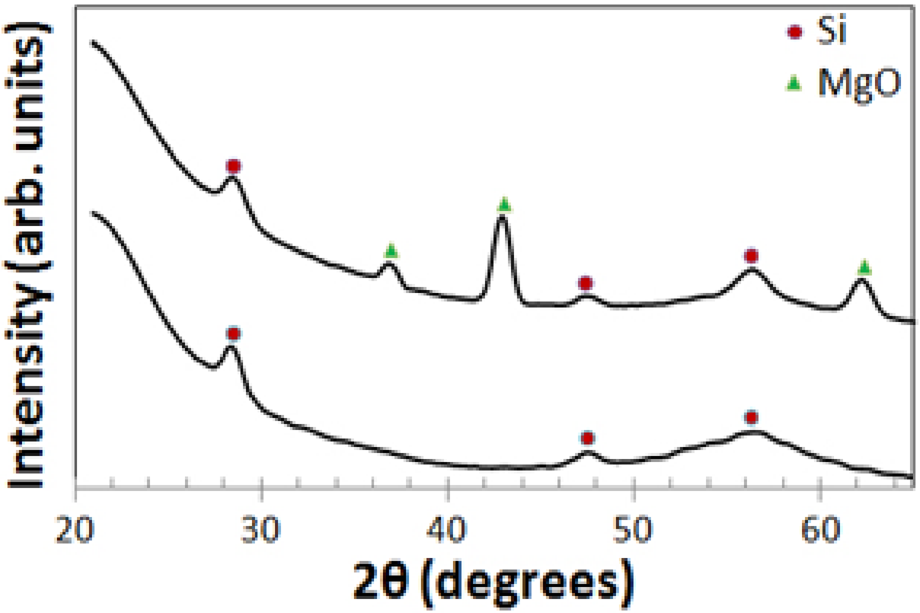
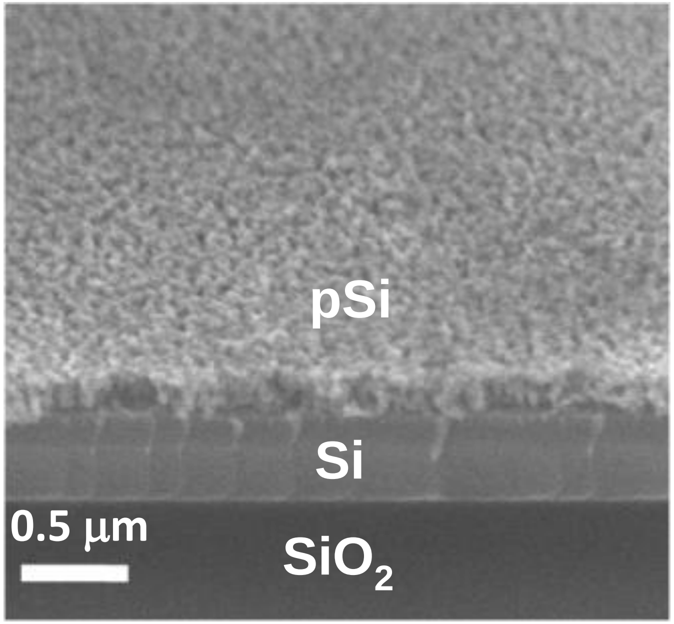
Porous Si on SOI via Magnesiothermic Rxn





X-ray Diffraction Analysis

Secondary electron image

(Selective reaction of Mg(g) with a SiO_2 layer present on Si, using Mg(g) from Mg_2Si; 750°C, 1 h)

Sandhage Group

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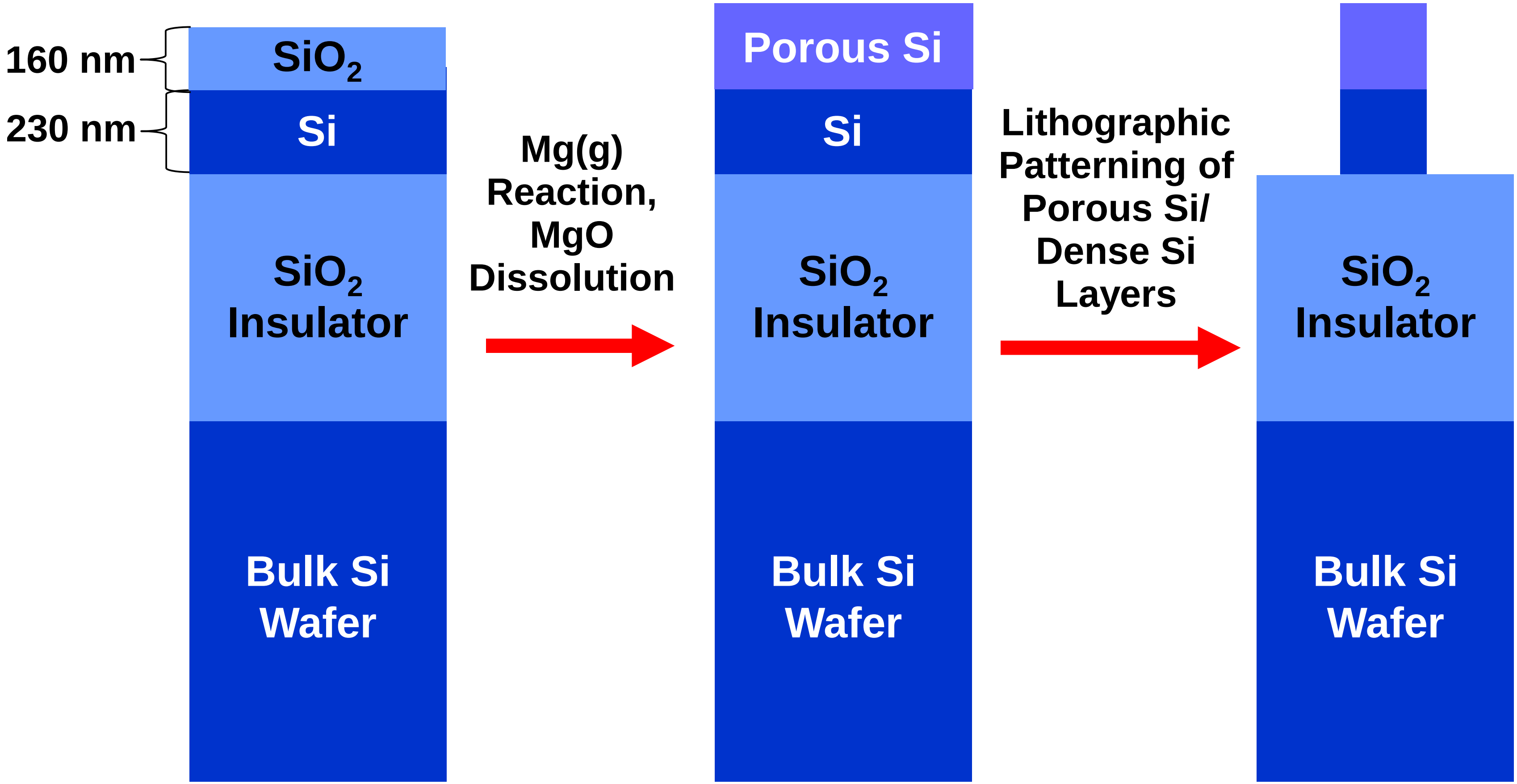
Magnesiothermic Rxn-then-Pattern Process



Oxidized SOI Wafer

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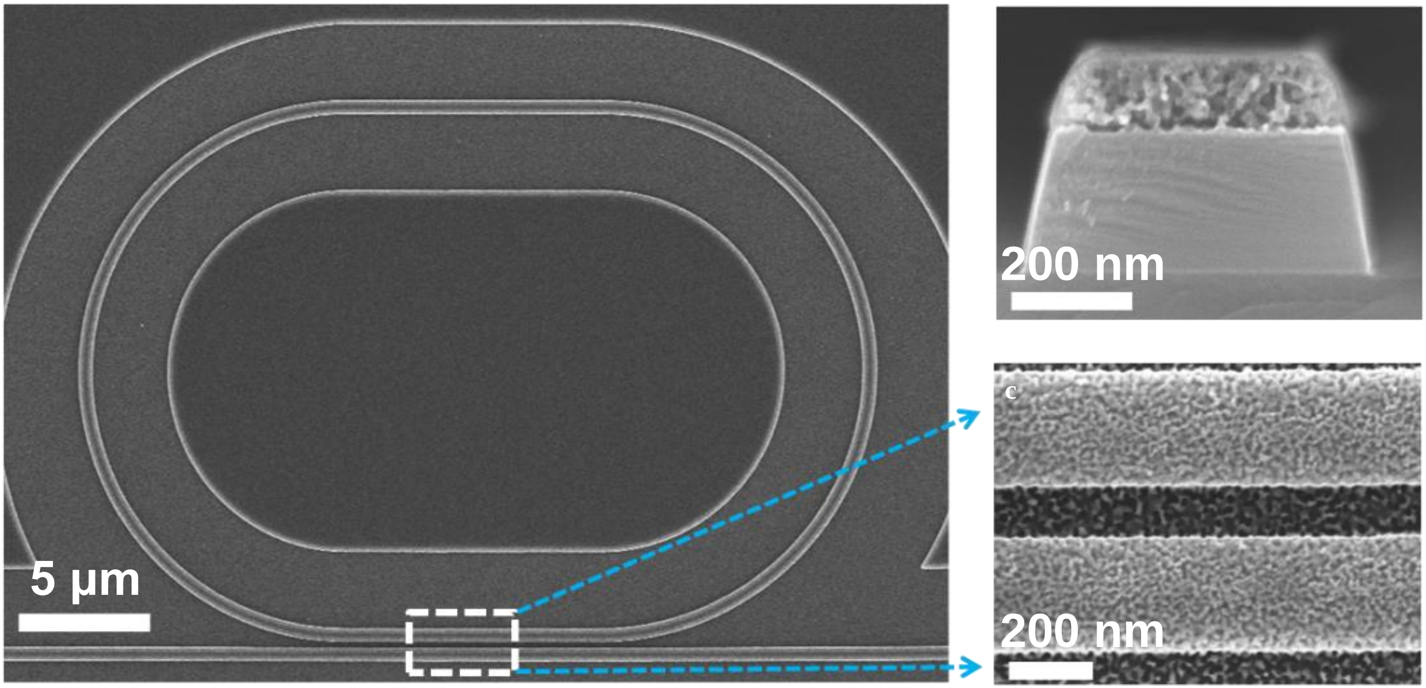
Porous Si on Micropatterned SOI Resonators



Secondary electron images

(with Adibi group, Georgia Tech)

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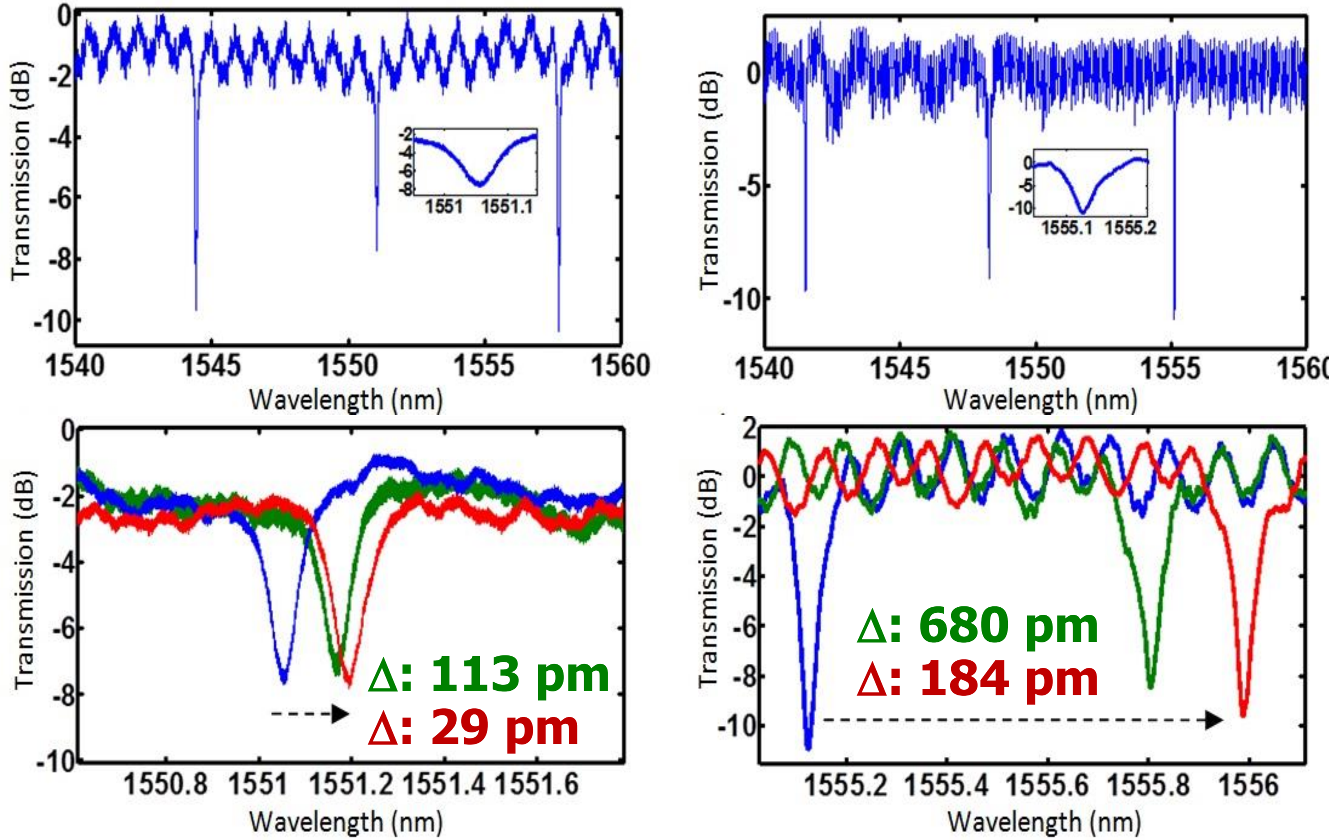
Sensitivity Enhancement with Porous Si

Without Porous Si | **With Porous Si**



FWHM = 68 pm

Q Factor = 23,000

Uncoated, APTES coated, NHS-biotin-coated

(with Adibi group, Georgia Tech)

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Shape-Preserving Chemical Transformation

- Fluid/Solid Reactions (displacement, additive, subtractive)
  - Macroscale/microstructured inorganic templates (liquid/solid reactions)
  - Microscale/nanostructured inorganic templates (gas/solid reactions)
- **Conformal Coating (inorganic, organic templates)**
  - **Surface sol-gel-based oxide deposition**
  - Protein-enabled oxide and oxide/organic deposition
  - Electroless metal deposition

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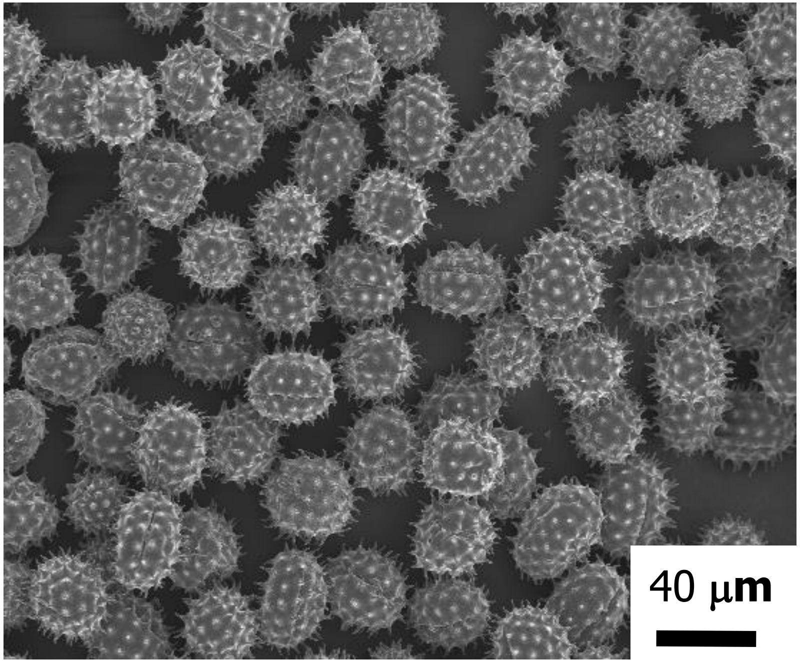
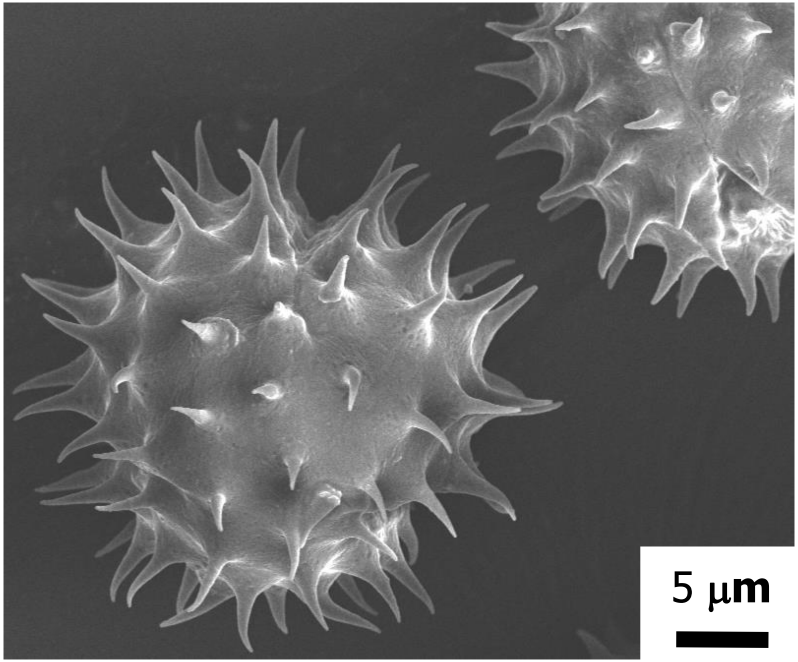
Pollen Grains

- 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

Sunflower (Helianthus annuus) Pollen





Secondary electron images

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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[1]
  - capillarity/wetting of pollenkitt[1]
- The pollen exine (outer layer) consists of sporopollenin, a robust polymer rich in carboxylic acids[2]

[1] H. Lin, et al., *Langmuir*, 29, 3102 (2013).
[2] E. Dominguez, et al., *Sec. Plant Reprod.*, 12, 171 (1999).

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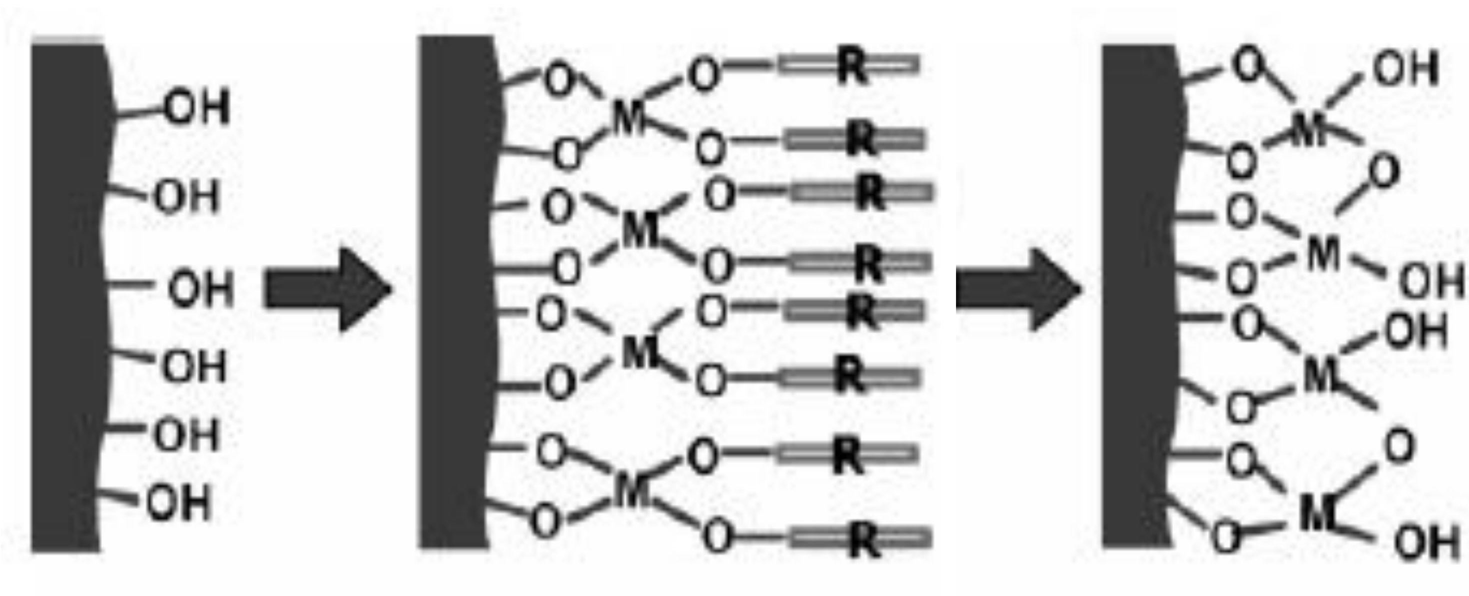
Surface Sol-Gel Processing

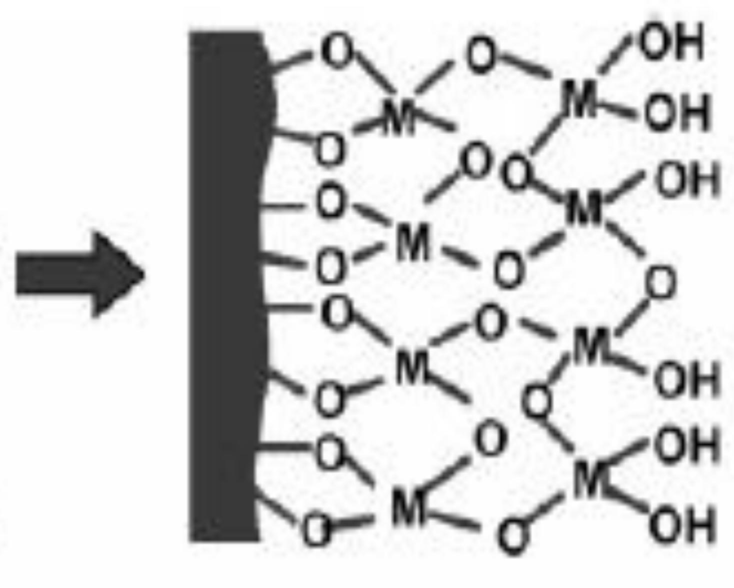


Chemisorption of Metal Alkoxide

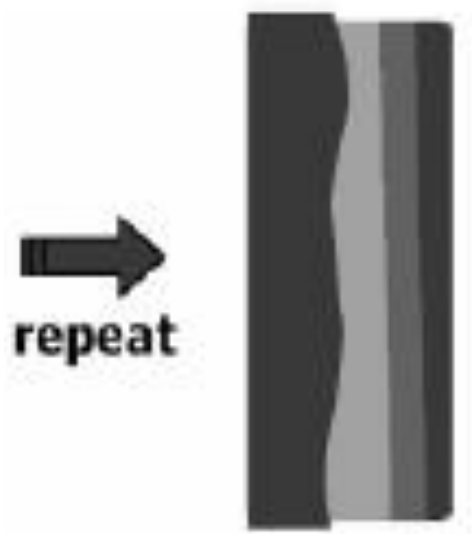
Water Hydrolysis

(obtained from S. Fujikawa, R. Takaki, T. Kunitake, *Langmuir*, 21, 8899 (2005))

Surface Sol-Gel Processing



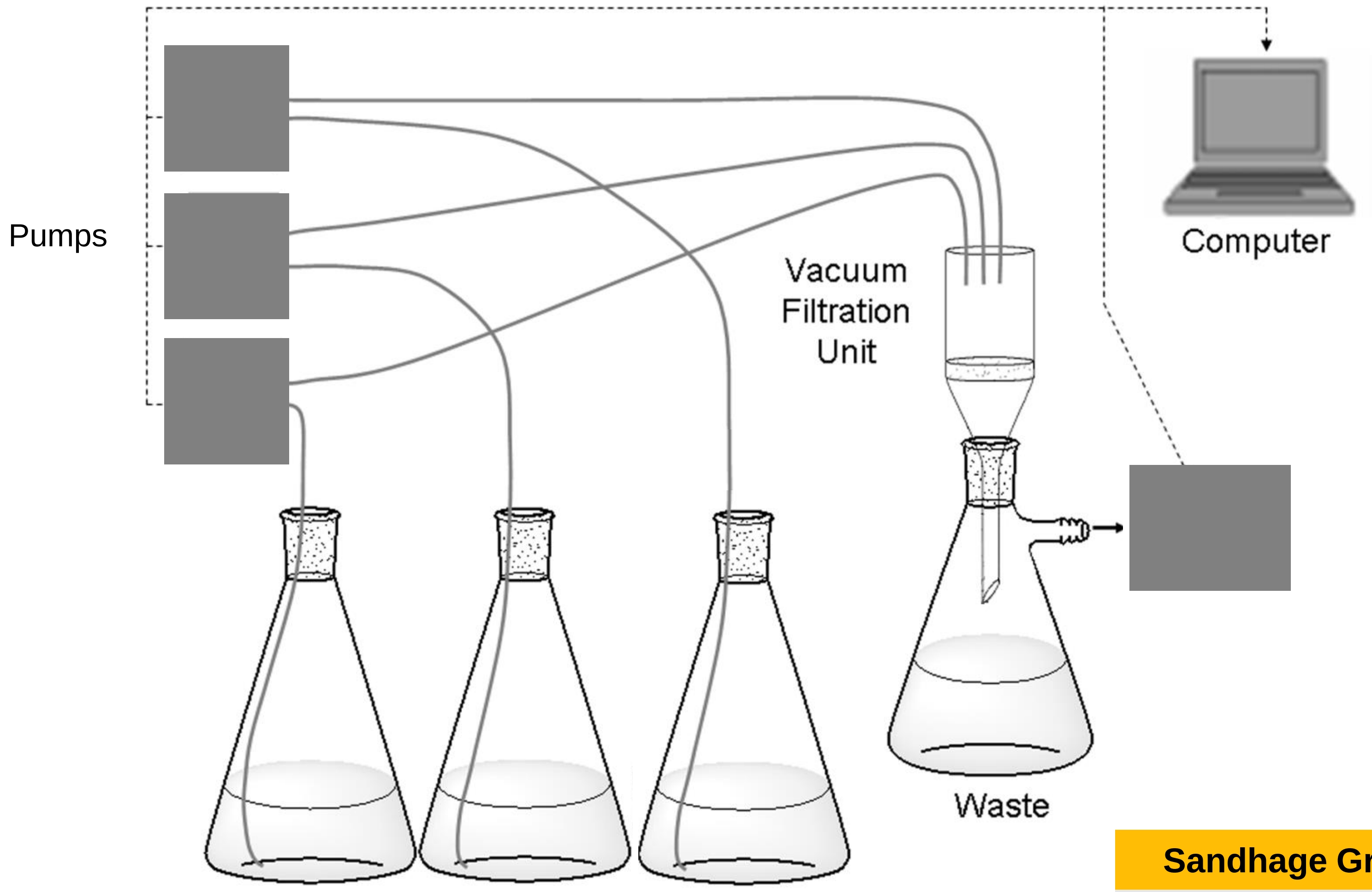
Resorption of Metal Alkoxide



Layering of Ultrathin Metal Oxide

(obtained from S. Fujikawa, R. Takaki, T. Kunitake, *Langmuir*, 21, 8899 (2005))

Automated Surface Sol-Gel System



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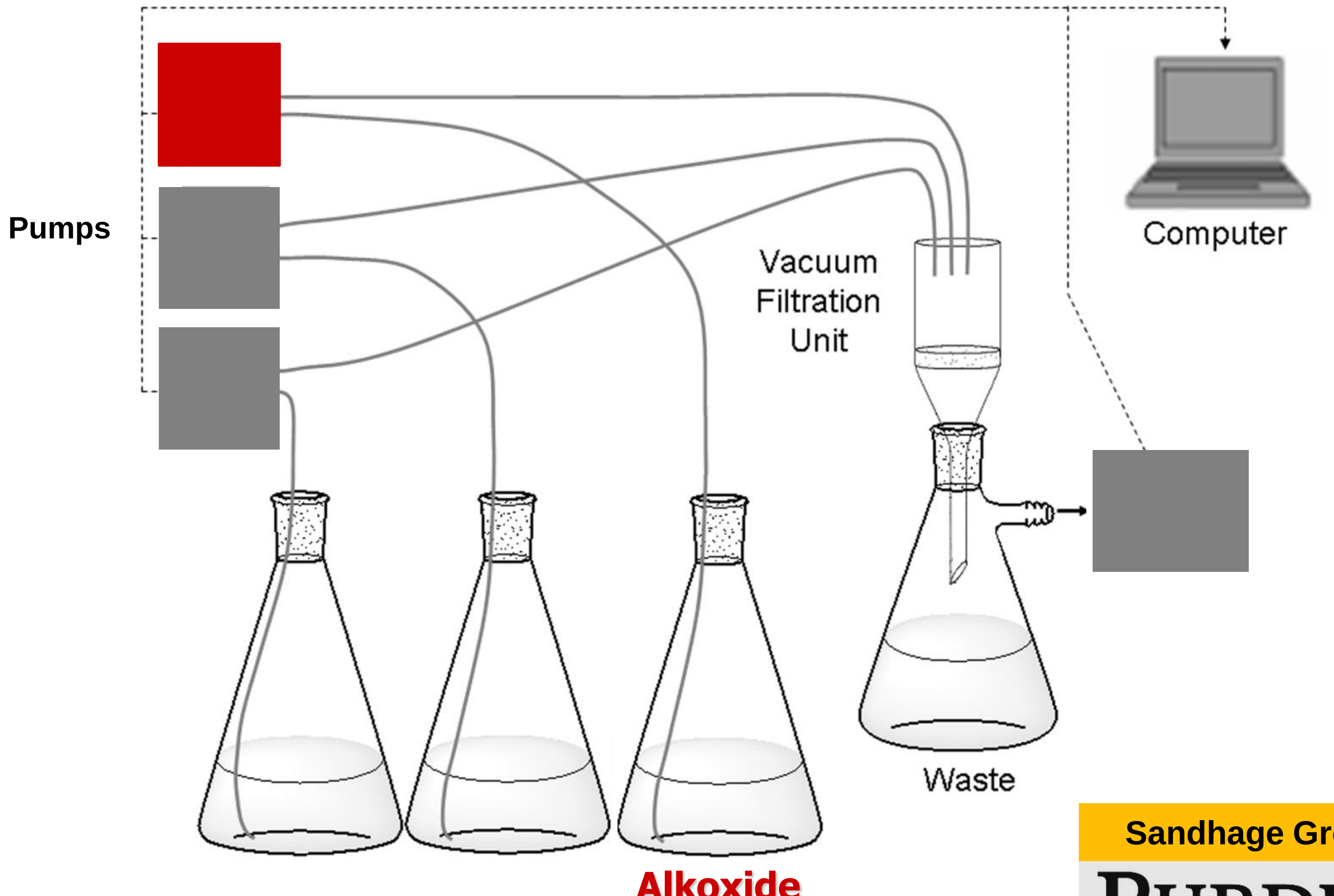
Automated Surface Sol-Gel System



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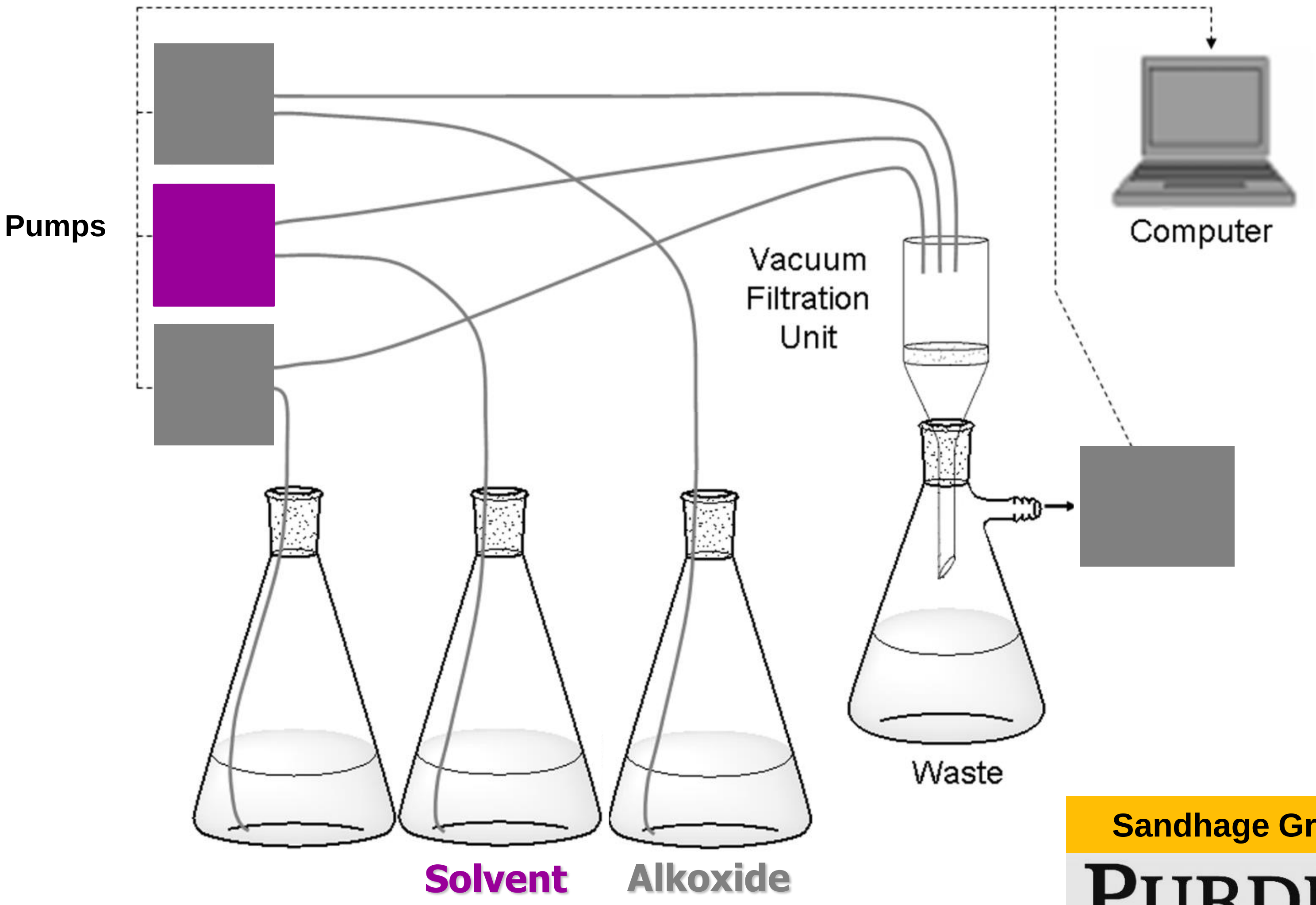
Automated Surface Sol-Gel System



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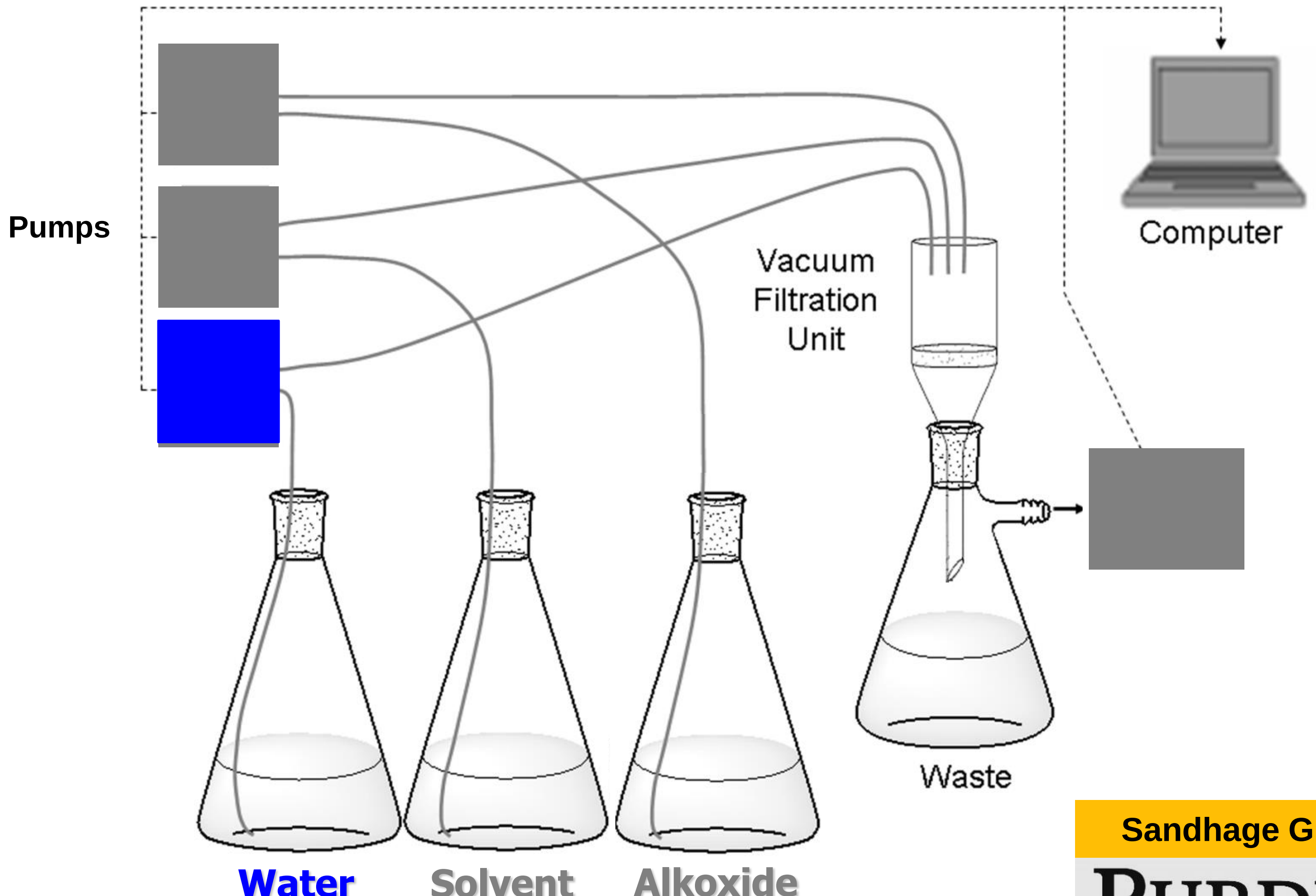
Automated Surface Sol-Gel System



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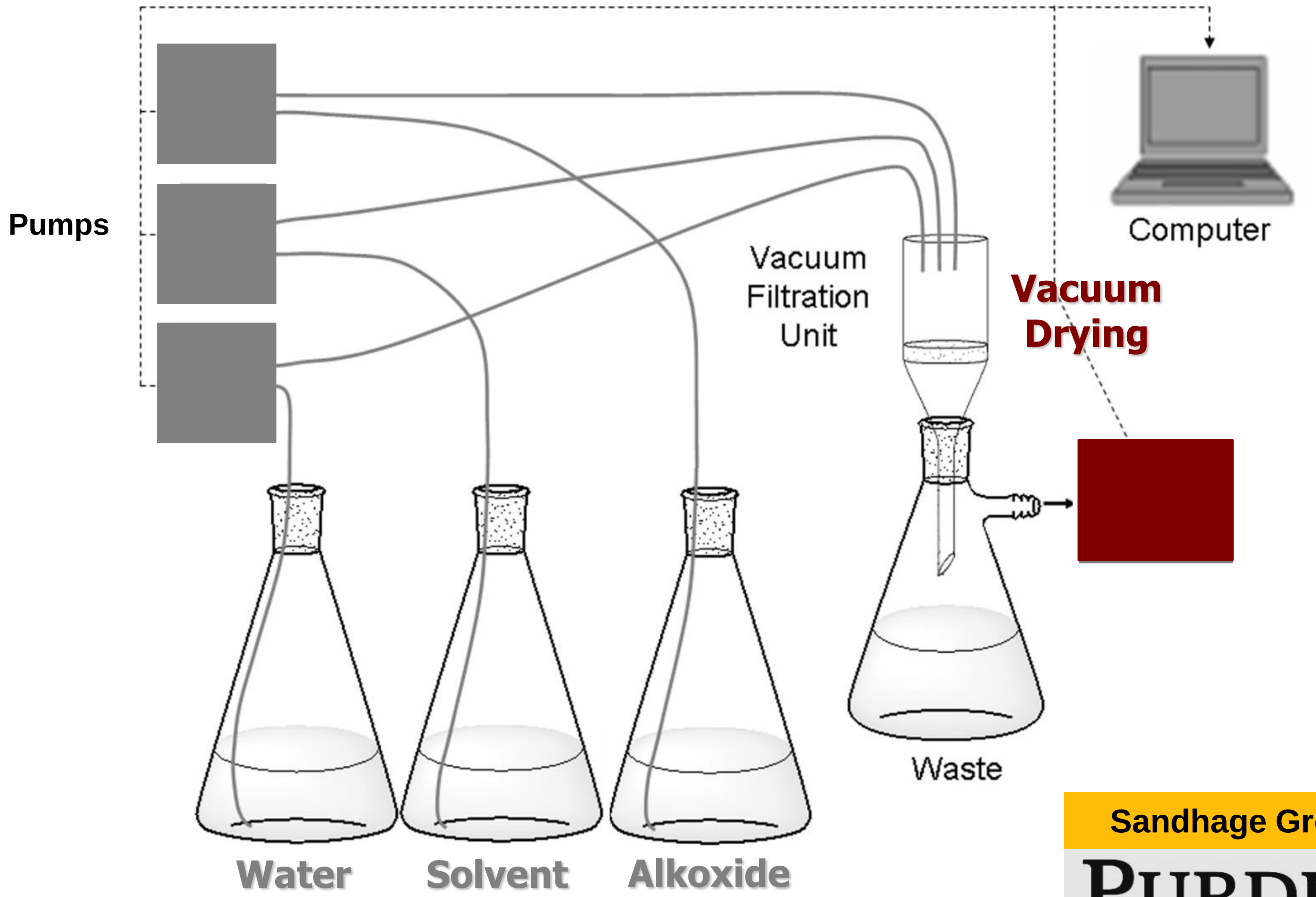
Automated Surface Sol-Gel System



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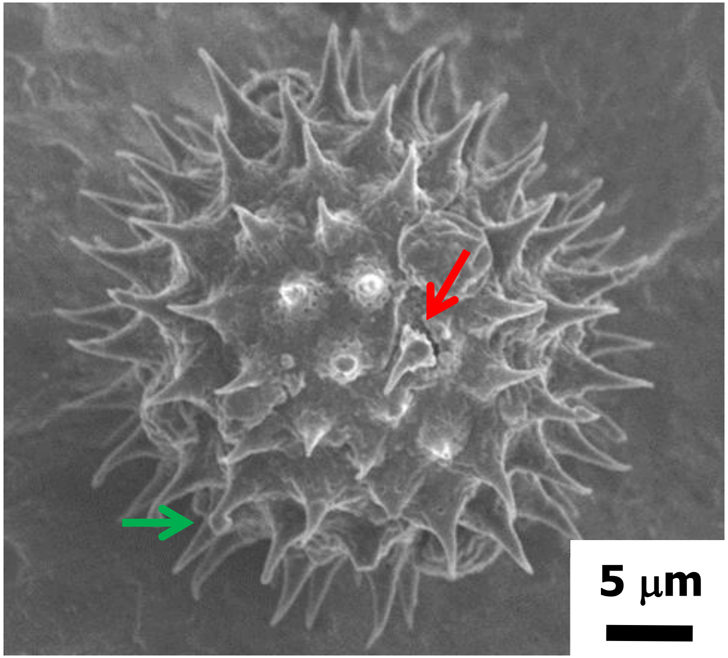
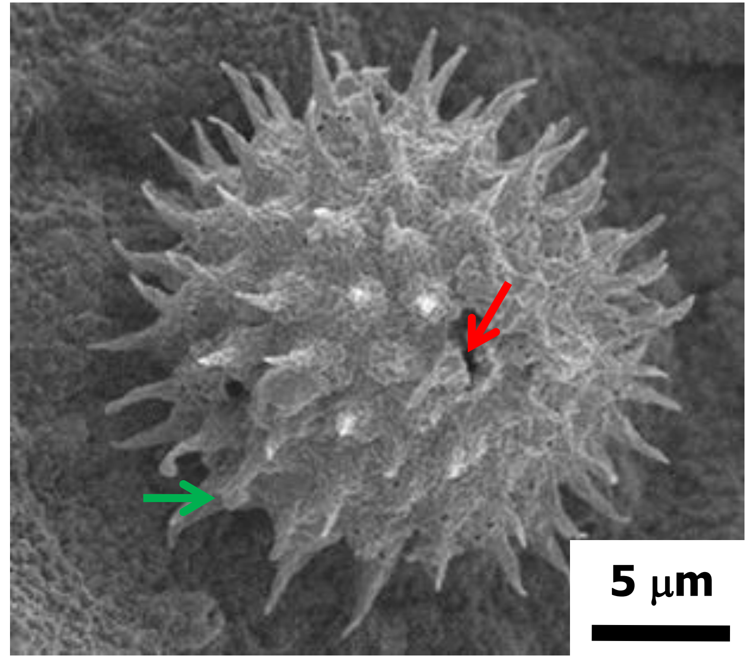
Iron Oxide Sunflower Pollen Replicas

Fe-O Coated Pollen



Fe_3O_4 Pollen Replica



Secondary electron images

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

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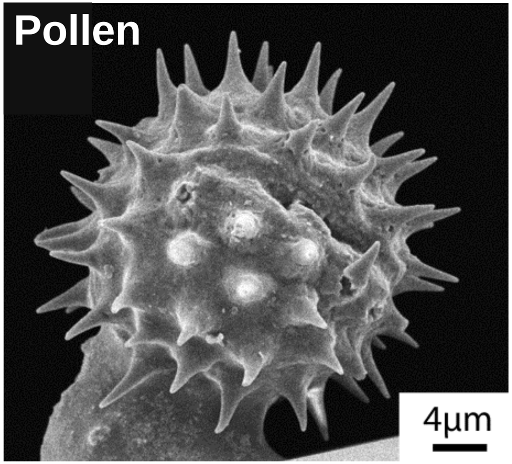
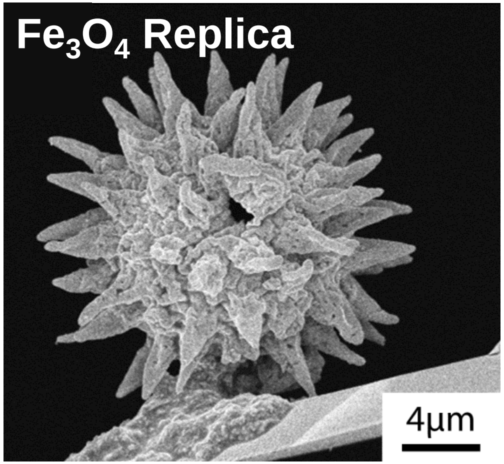
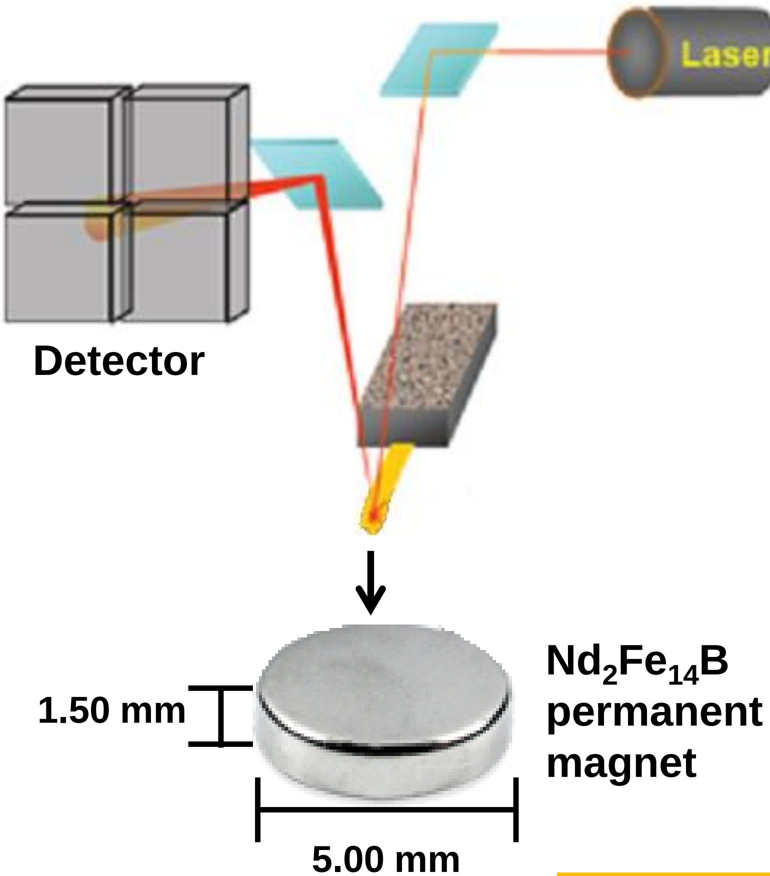
Adhesion Testing of Pollen and Pollen Replicas







(with Meredith group, Georgia Tech)

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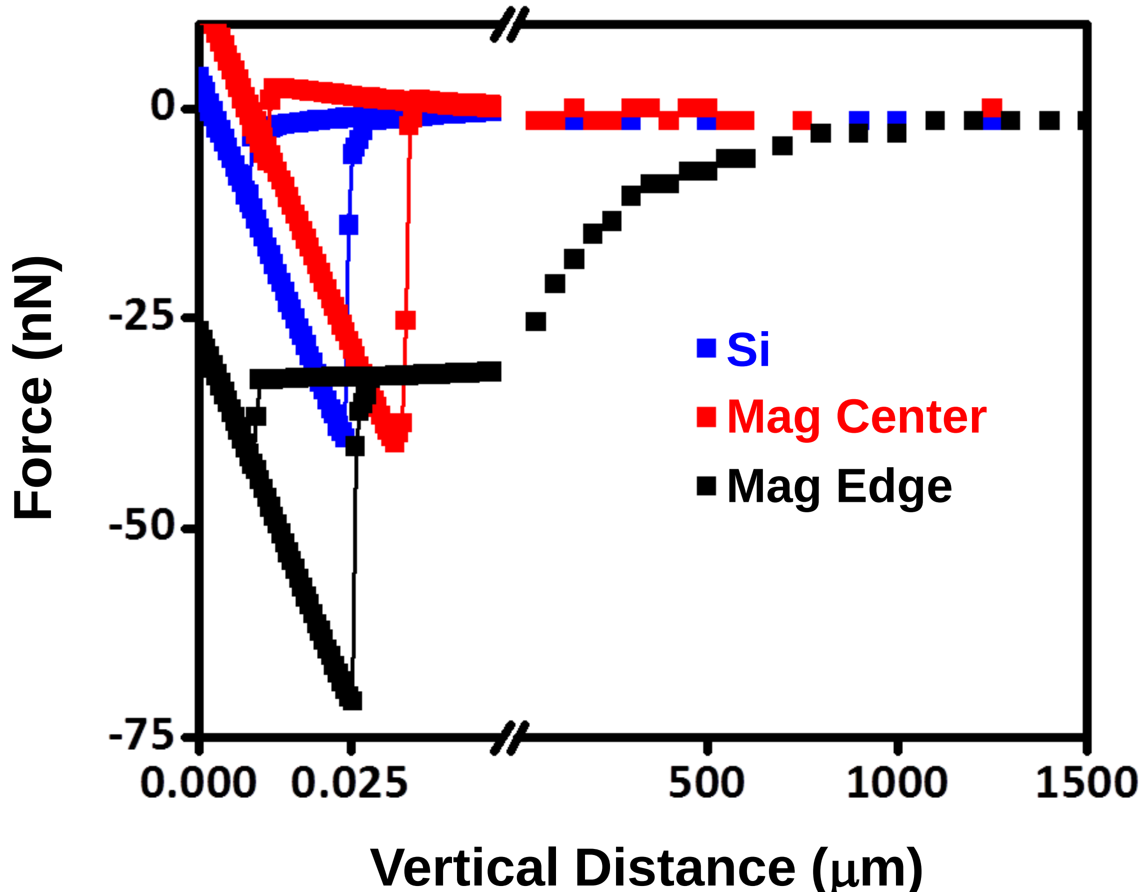
Multi-modal Adhesion of Fe_3O_4 Replicas



(with Meredith group, Georgia Tech)

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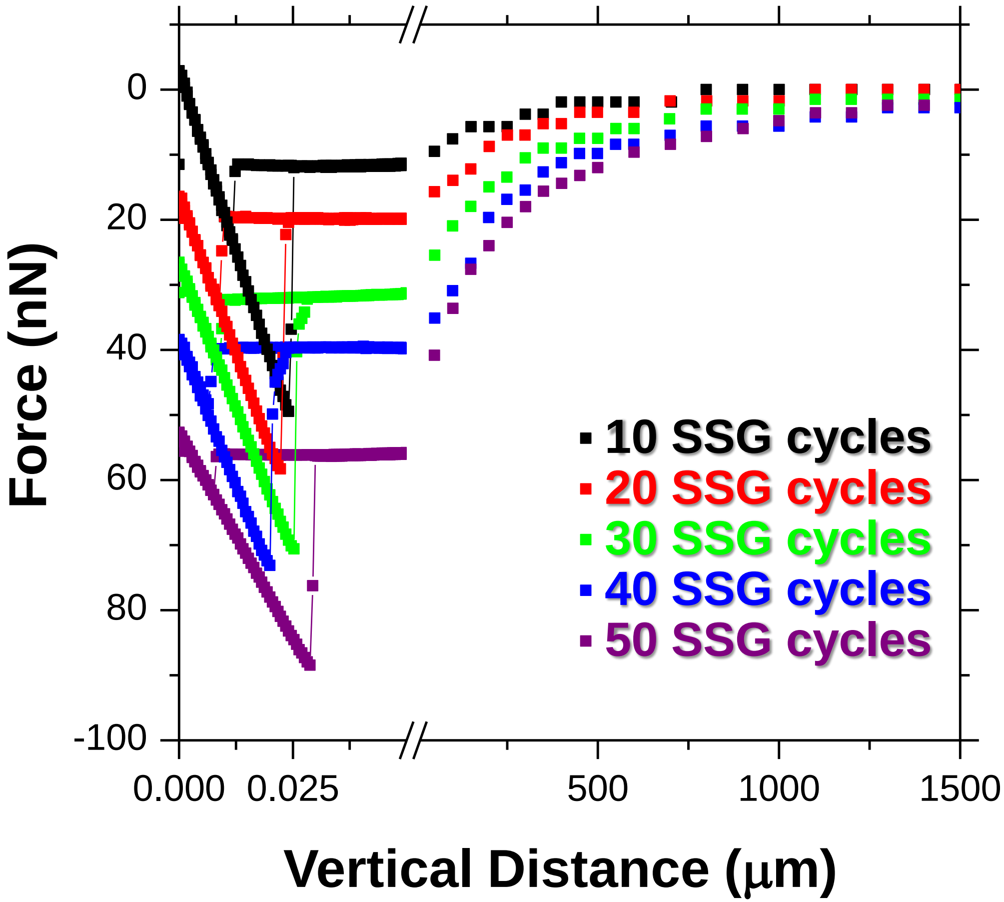
Tailorable Long Range Magnetic Adhesion



(with Meredith group, Georgia Tech)

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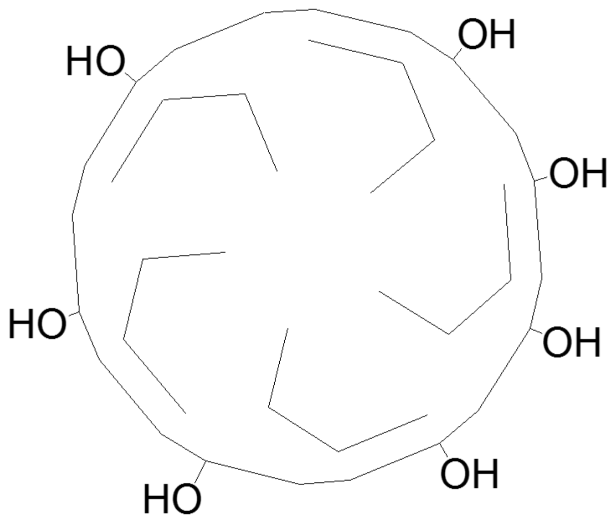
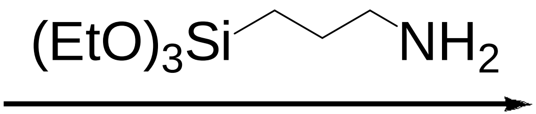
Surface Functionalization of Frustules

(with Marder group, Georgia Tech)





(3-aminopropyl)triethoxy-silane in NH_4OH (aq.), reflux

Diatom frustule with a modest concentration of -OH groups

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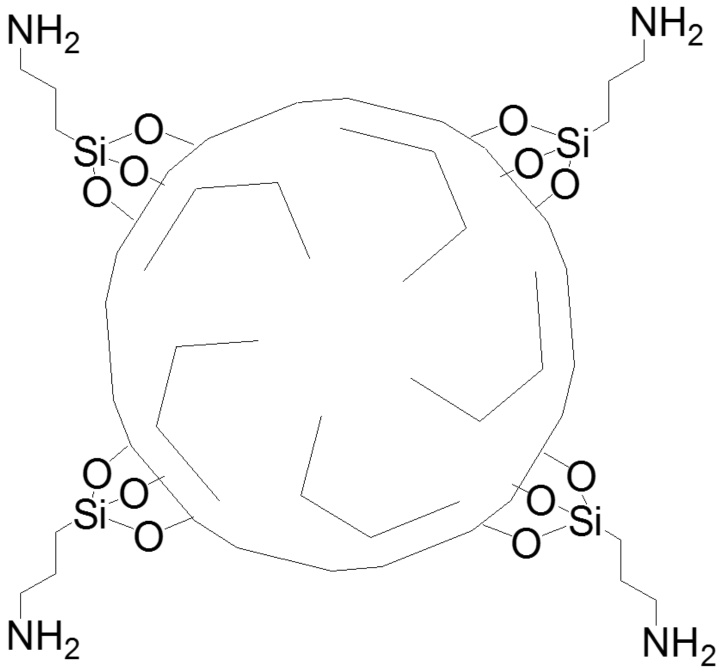
Surface Functionalization of Frustules



Aminosilanized diatom frustule with a modest concentration of -NH_2 groups

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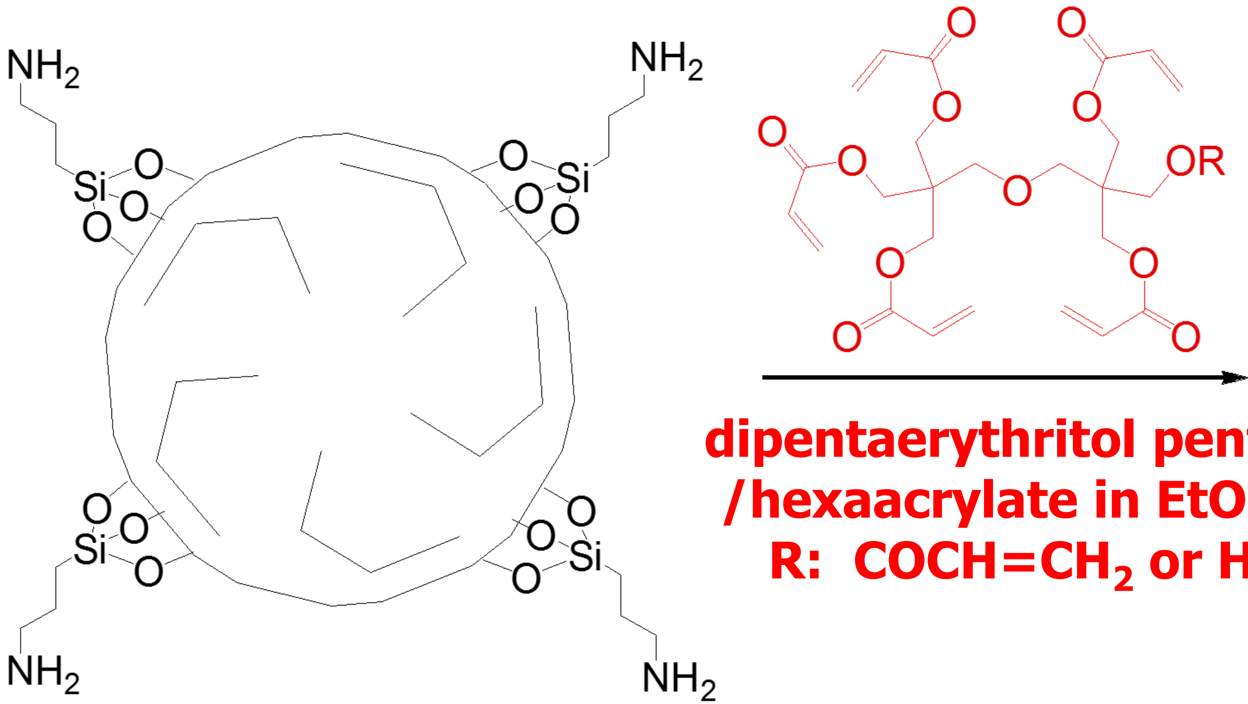
Surface Functionalization of Frustules



Step A

dipentaerythritol penta-/hexaacrylate in EtOH; R: $COCH{=}CH_2$ or H

Aminosilanized diatom frustule with a modest concentration of $-NH_2$ groups

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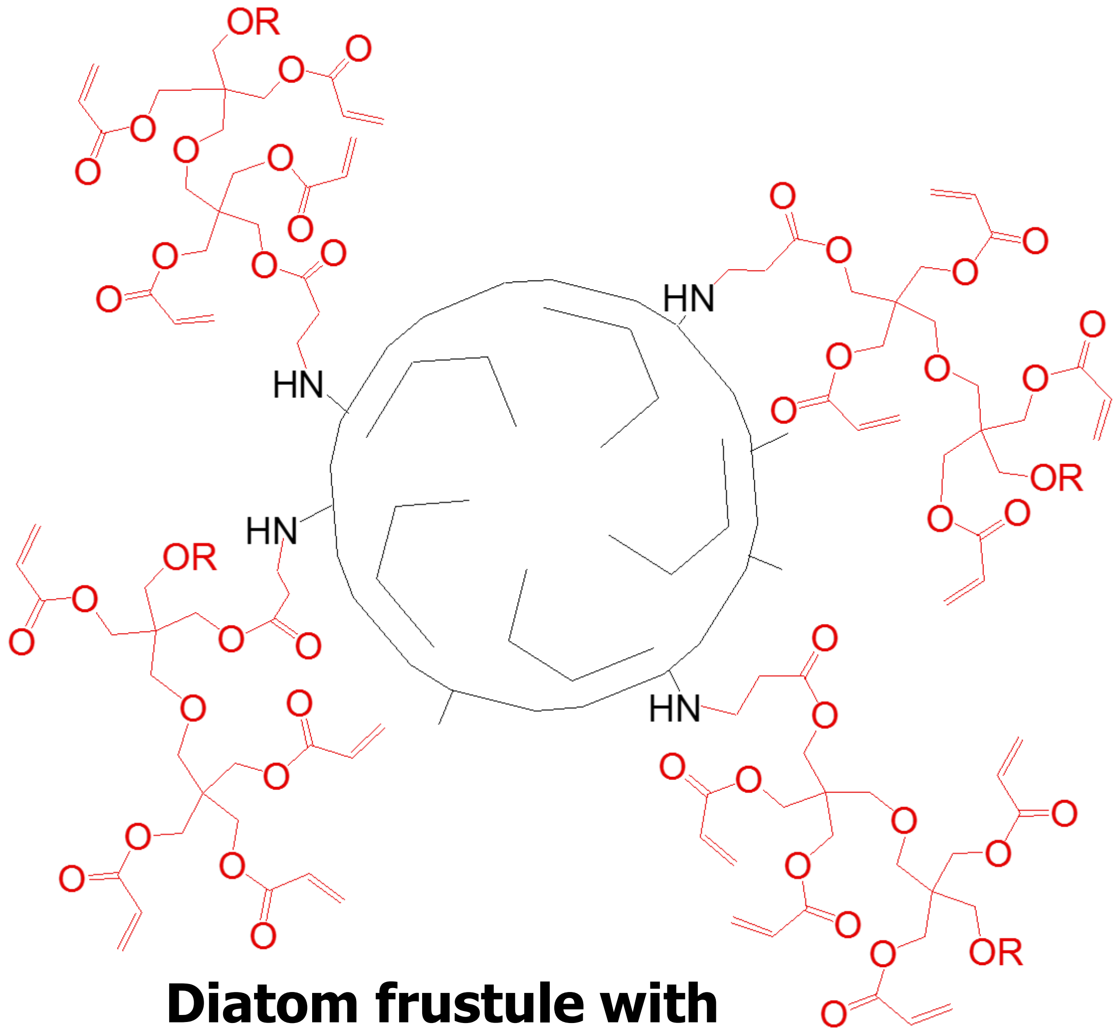
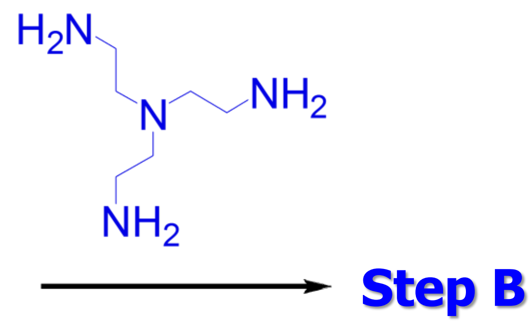
Surface Functionalization of Frustules



Diatom frustule with polyacrylate groups



tris(2-aminoethyl) amine in EtOH

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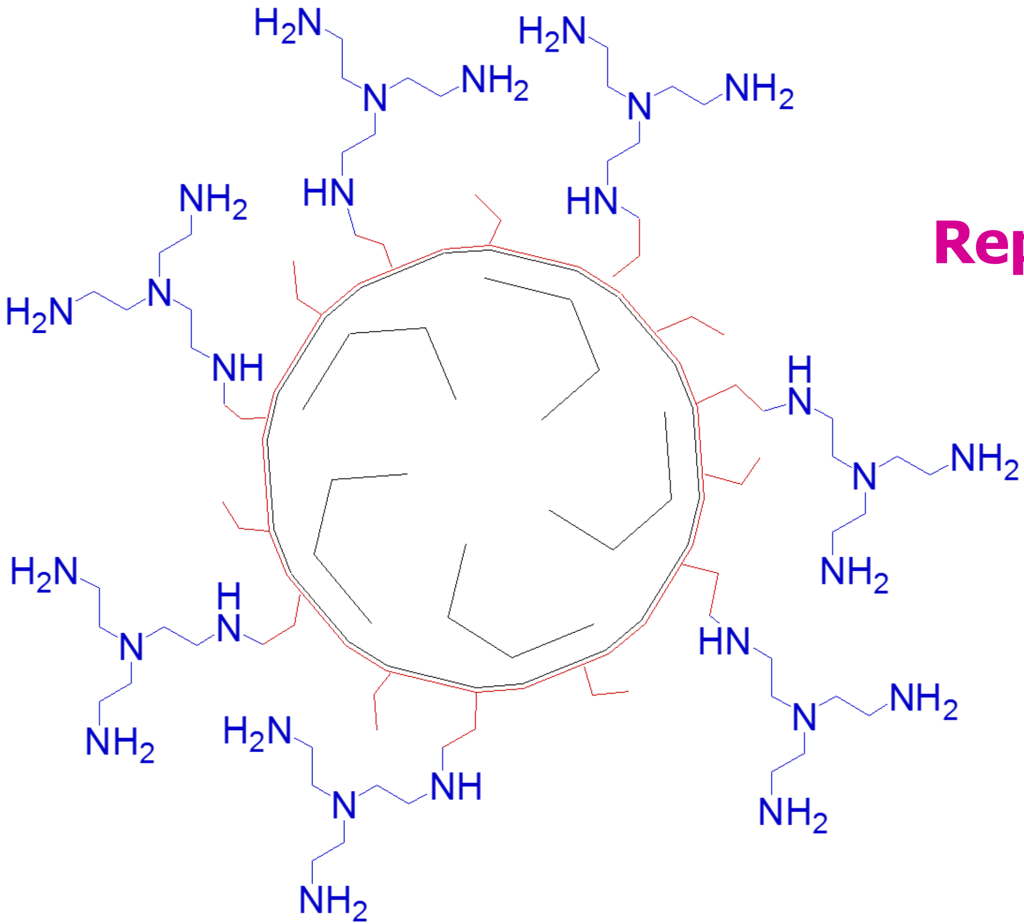
Surface Functionalization of Frustules



Repeat steps A and B

Diatom frustule with polyamine groups

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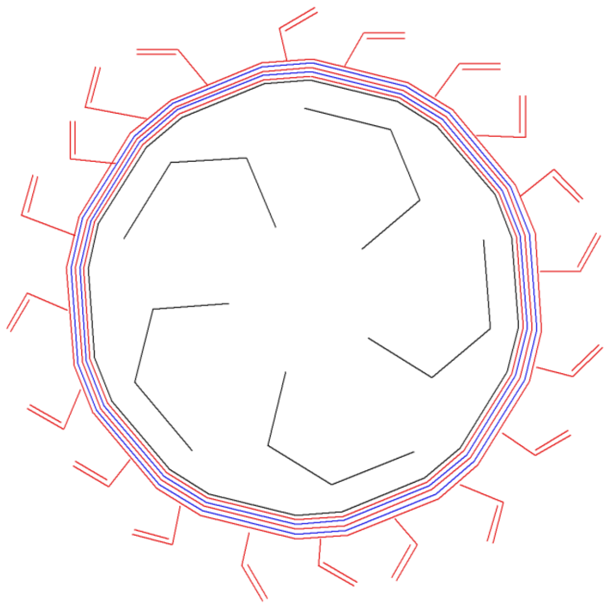
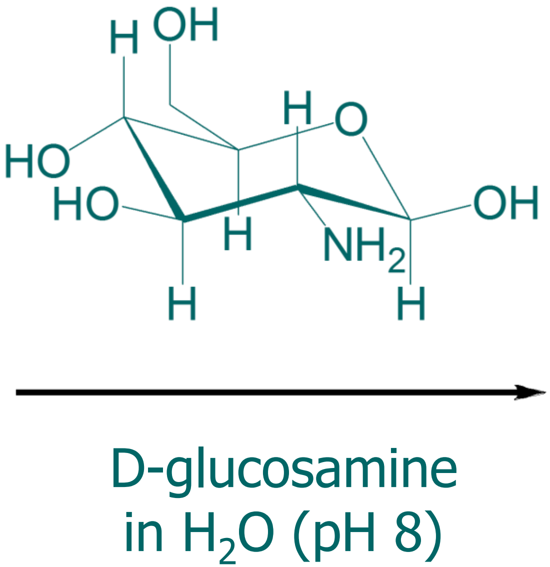
Surface Functionalization of Frustules





Diatom frustule with dendritic branching of polyamine and polyacrylate groups

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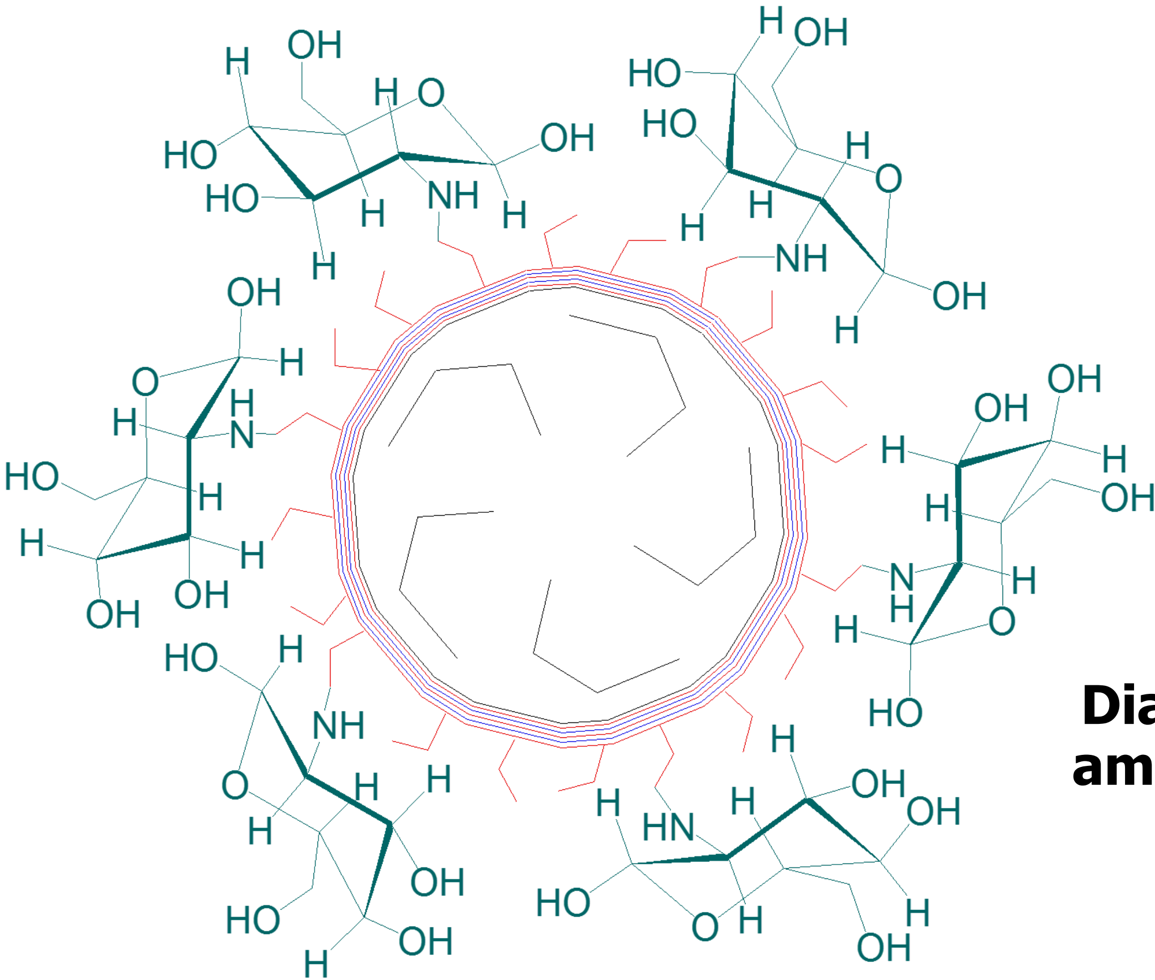
Surface Functionalization of Frustules



Diatom frustule with amplified -OH groups

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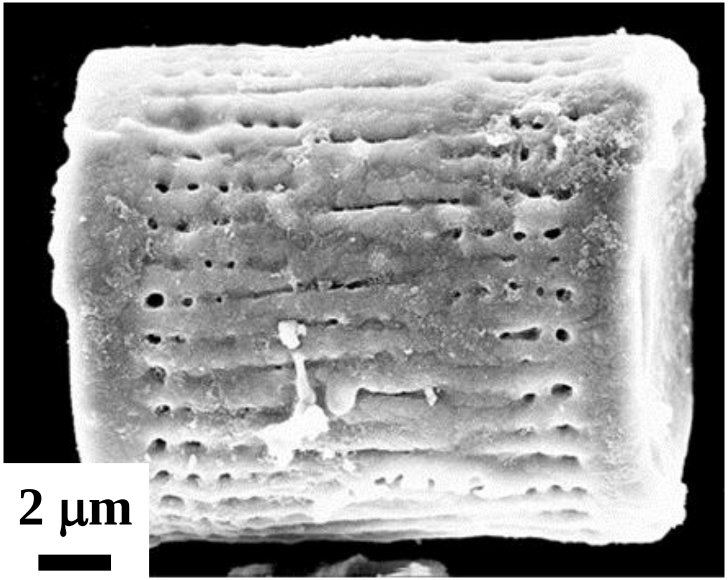
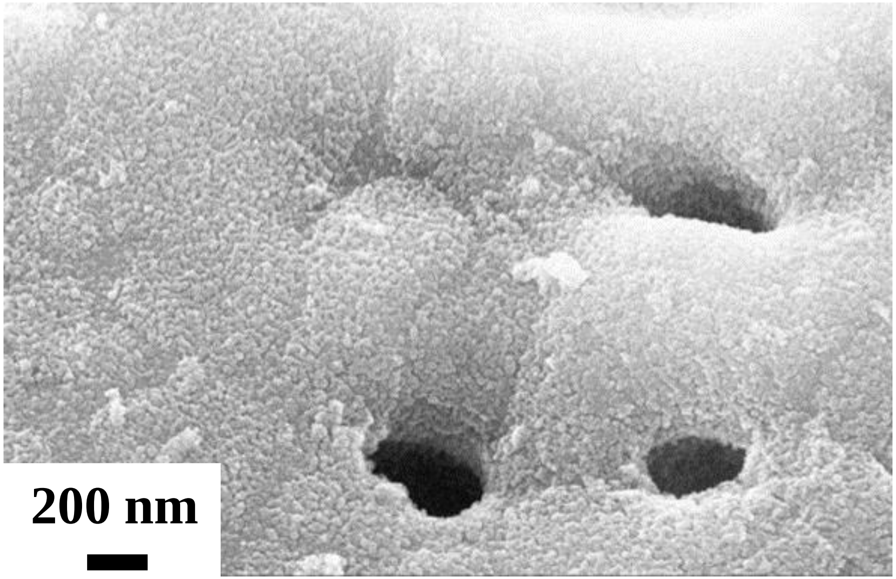
Fe_3O_4-coated Diatom Frustules





Secondary electron images

(21 SSG cycles involving Fe(III) isopropoxide, 550°C/2 h in Fe/Fe_3O_4 Rhines pack)

(with Marder and Perry groups, Georgia Tech)

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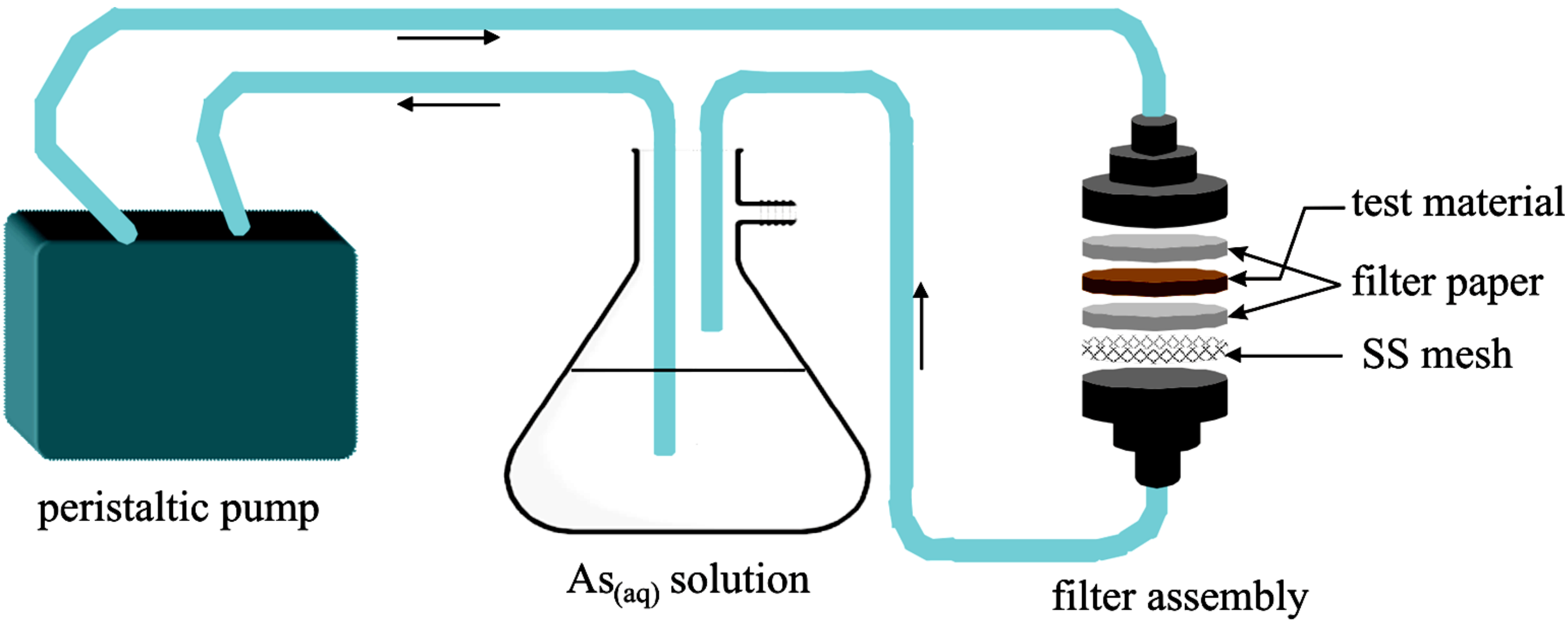
As Adsorption Experiments



	SSA (m²/g)	Porosity (vol%)
Commercial Fe_3O_4 (CM):	44.0	68
Fe_3O_4 Diatoms (MD):	4.7	55

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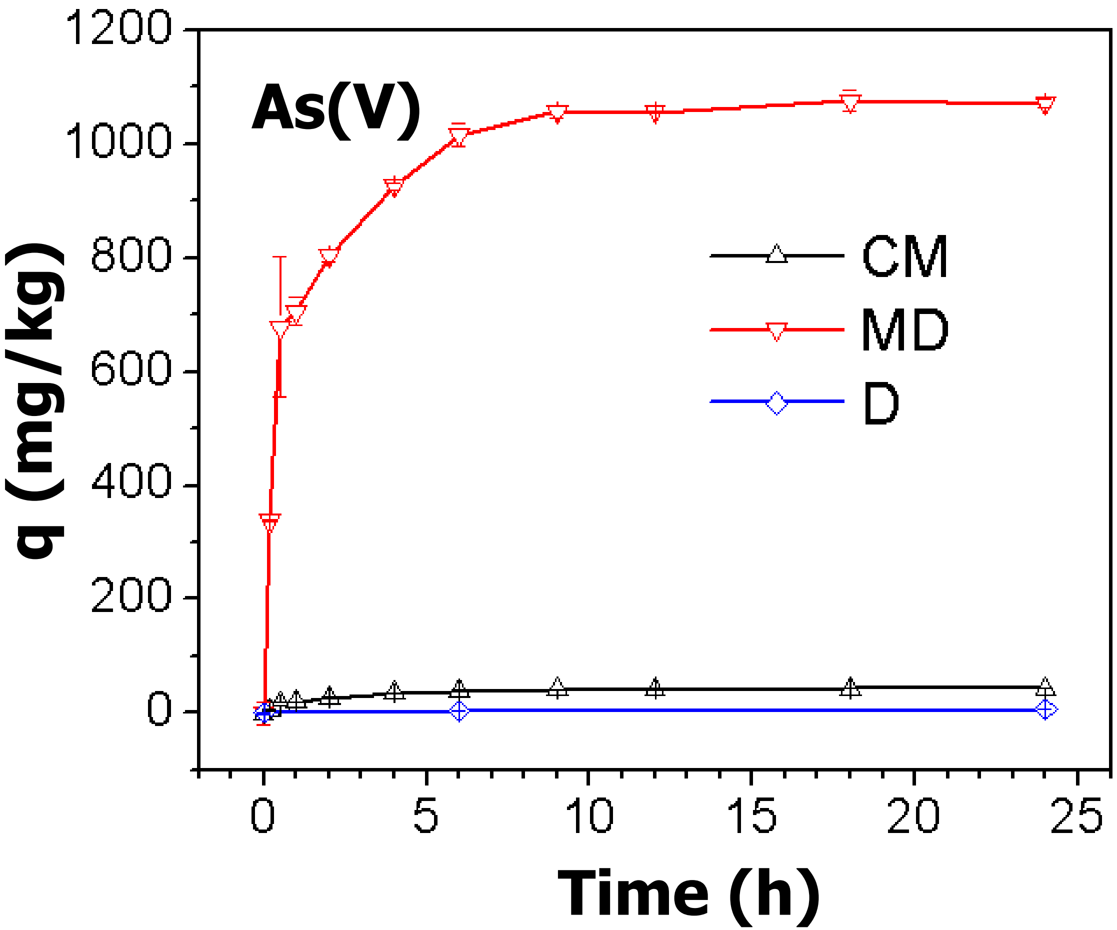
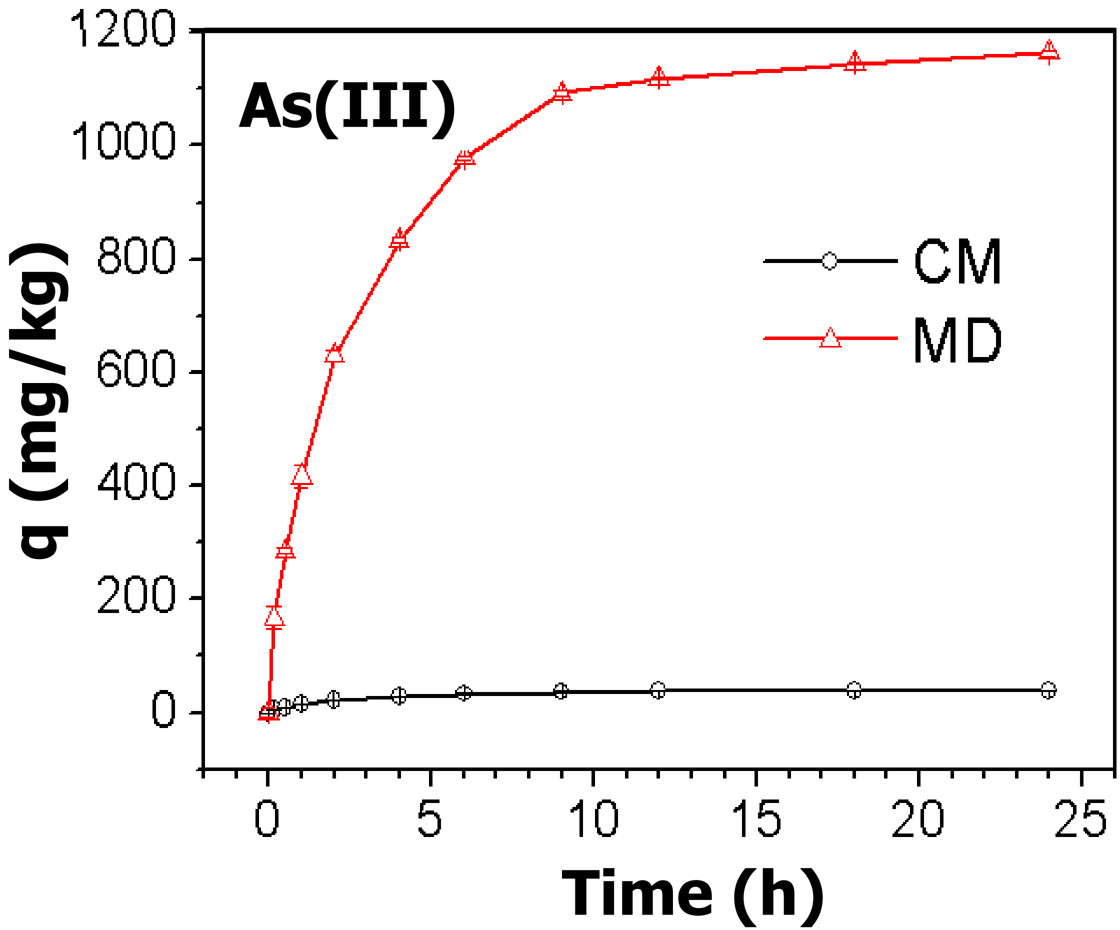
As Removal from Water w/Fe_3O_4-coated Frustules



	SSA (m^2/g)	Porosity (vol%)
CM:	44.0	68
MD:	4.7	55

(with Marder and Parry groups, Georgia Tech)

As Removal from Water w/Fe_3O_4-coated Frustules



	SSA (m^2/g)	Porosity (vol%)
CM:	44.0	68
MD:	4.7	55

(with Marder and Parry groups, Georgia Tech)

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Summary

- ***Shape-preserving liquid/solid and gas/solid reactions*** **have been used to convert synthetic and biogenic inorganic structures (porous WC preforms, diatom frustules, micropatterned Si) into 3-D positive replicas comprised of a variety of inorganic materials:**

$$WC(s) + \{Zr\} => ZrC(s) + W(s)$$

$$SiO_2(s) + 2Mg(g) => 2MgO(s) + Si(s) => Si(s)$$

- **Microscale 3-D bio-organic structures (e.g., pollen grains, butterfly scales) have been converted into negative replicas of functional oxides via *layer-by-layer conformal coating and thermal treatment*:**
  - **Surface sol-gel oxide deposition**
  - **Organic pyrolysis and oxide crystallization**

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Summary

- **Such chemically-tailored, 2-D or 3-D synthetic and biogenic structures can be attractive for use as:**
  - **high surface area electrodes (e.g., for batteries, fuel cells)**
  - **highly absorptive materials (e.g., for water or chemical purification)**
  - **patterned optical structures for tailored transmission or reflection (e.g., for sensors, anti-counterfitting, IR focusing)**
  - **particles with tailored magnetism and adhesion (e.g., for tagging, labelling, magnetic separation)**
  - **high temperature robust components (e.g., solid-fuel rocket nozzles, pumps, heat exchangers, engine components)**

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