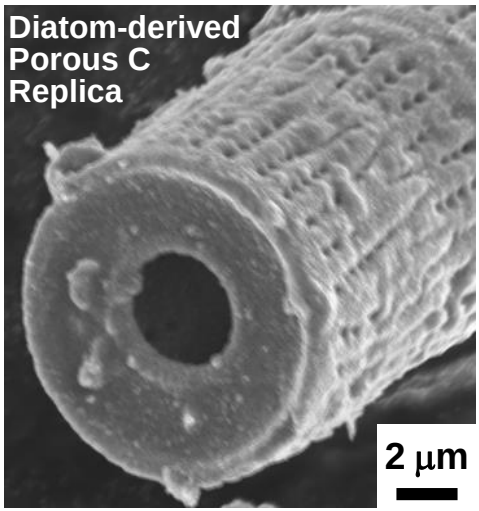
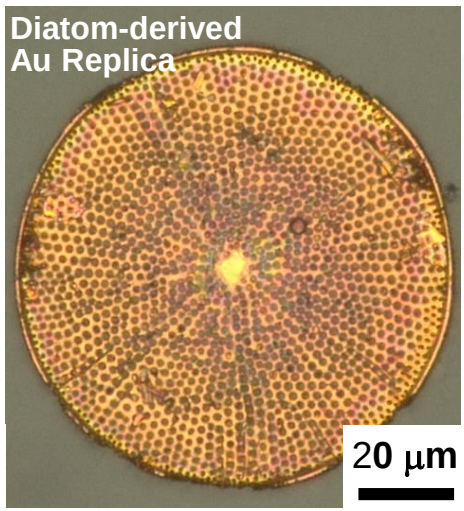
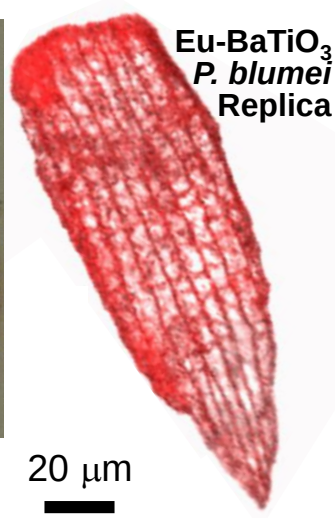
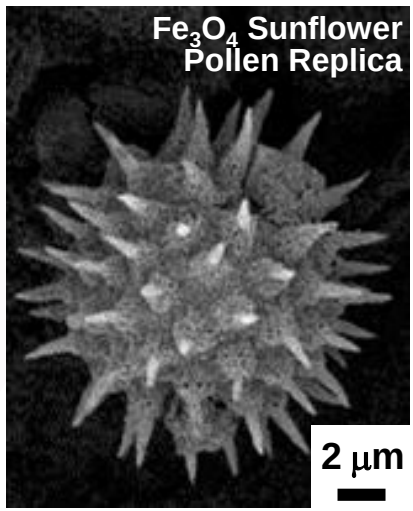
Biomaterials Alchemy: Changing the Chemistries, but not Shapes, of Biogenic Structures









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West Lafayette, IN

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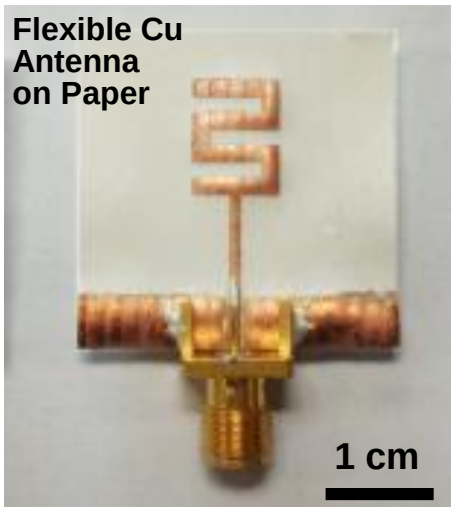
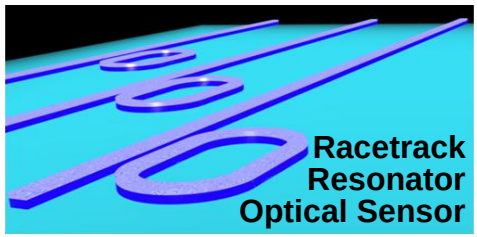
Materials Alchemy: Changing the Chemistries, but not Shapes, of Synthetic Structures





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Coating and Conversion of Pollen Grains, Butterfly Scales, and Diatom Frustules with/into Fe_3O_4, SnO_2, TiO_2, Zn_2SiO_4, $BaTiO_3$ via Computor-Automated, Layer-by-Layer, Surface Sol-Gel Deposition

I. J. Gomez, W. B. Goodwin, D. Sabo, Z. J. Zhang, K. H. Sandhage*, J. C. Meredith*, *J. Mater. Chem. C*, 3 (3) 632 (2015); W. B. Goodwin, I. J. Gomez, Y. Fang, J. C. Meredith, K. H. Sandhage, *Chem. Mater.*, 25, 4529 (2013); J. P. Vernon, N. Hobbs, A. Lethbridge, P, Vukusic, D. D. Deheyn, K. H. Sandhage, *J. Mater. Chem.*, 22, 10435 (2012); J. P. Vernon, Y. Fang, Y. Cai, J. H. Sandhage, *Angew. Chem. Int. Ed.*, 49, 7765 (2010); G. Wang, Y. Fang, P. Kim, A. Hayek, M. R. Weatherspoon, J. W. Perry, K. H. Sandhage, S. R. Marder, S. C. Jones, *Adv. Funct. Mater.*, 19, 2768 (2009); M. R. Weatherspoon, Y. Cai, M. Crne, M. Srinivasarao, K. H. Sandhage, *Angew. Chem. Int. Ed.*, 47, 7921 (2008); M. R. Weatherspoon, M. B. Dickerson, G. Wang, Y. Cai, S. Shian, S. C. Jones, S. R. Marder, K. H. Sandhage, *Angew. Chem. Int. Ed.*, 46, 5724 (2007).

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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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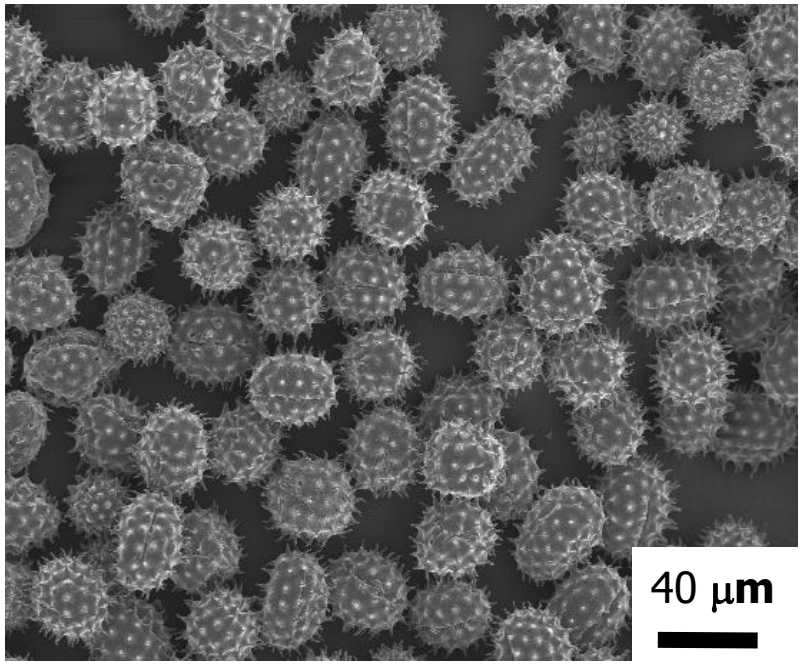
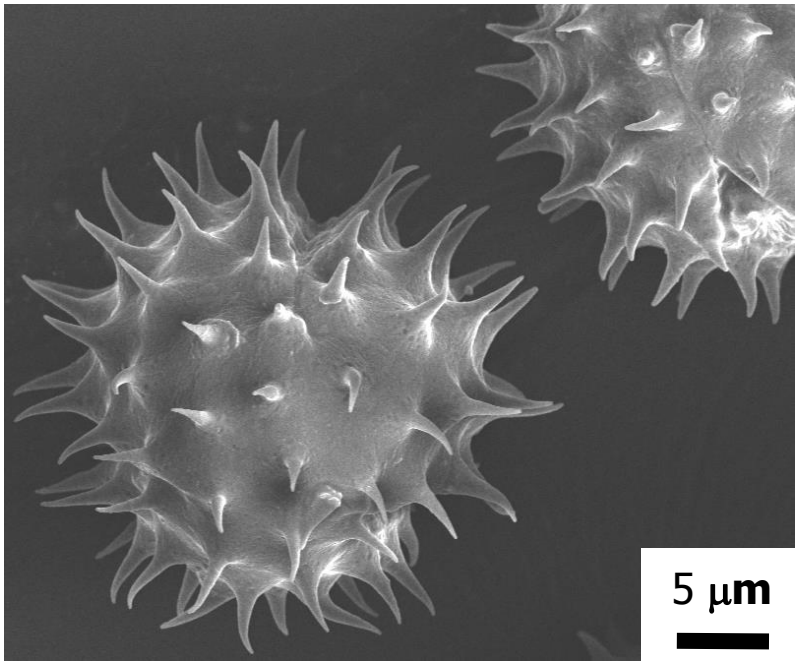
Sunflower (Helianthus annuus) Pollen





Secondary electron images

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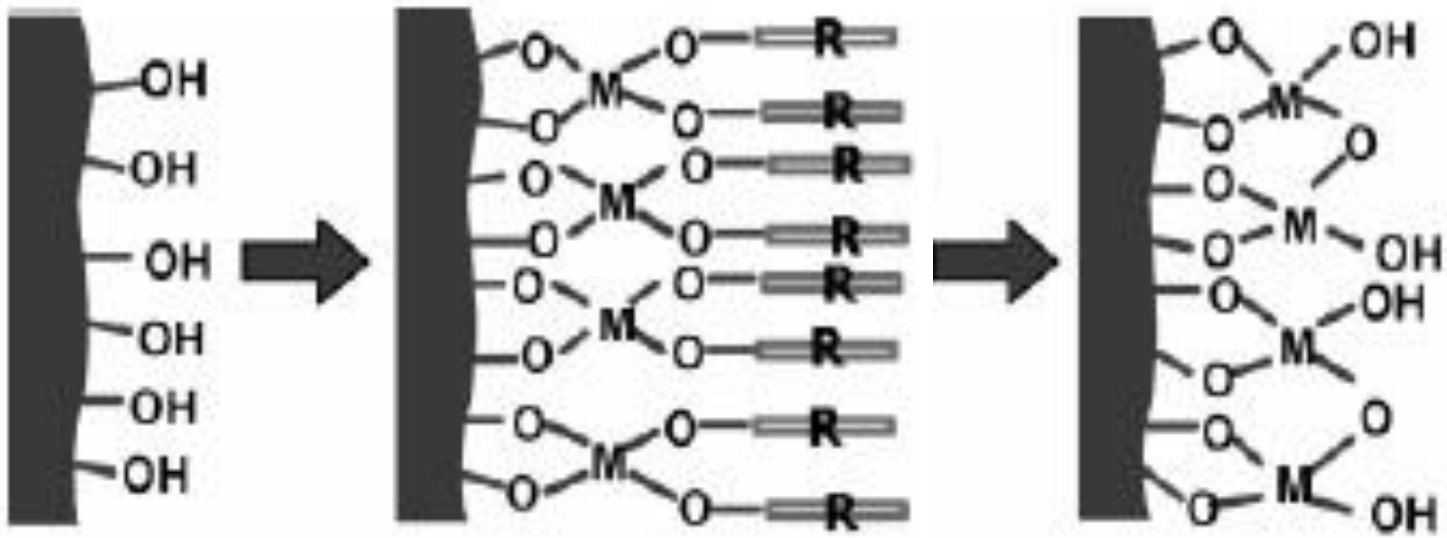
Surface Sol-Gel Processing

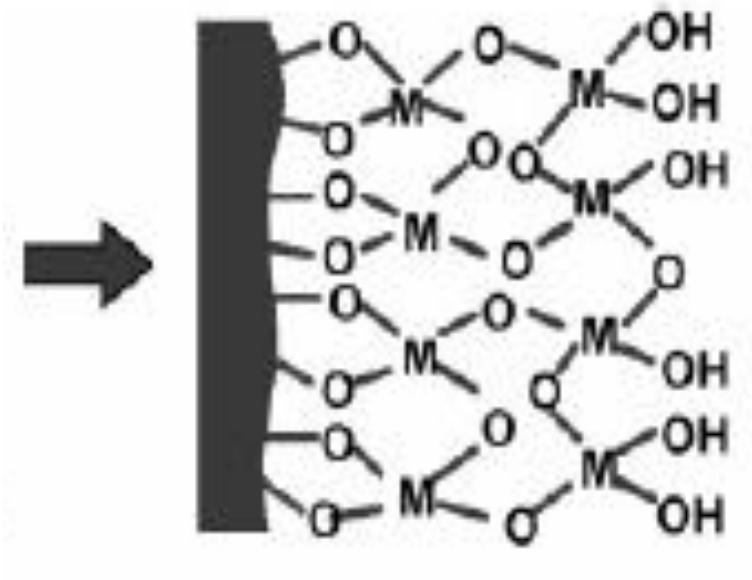


Chemisorption of Metal Alkoxide

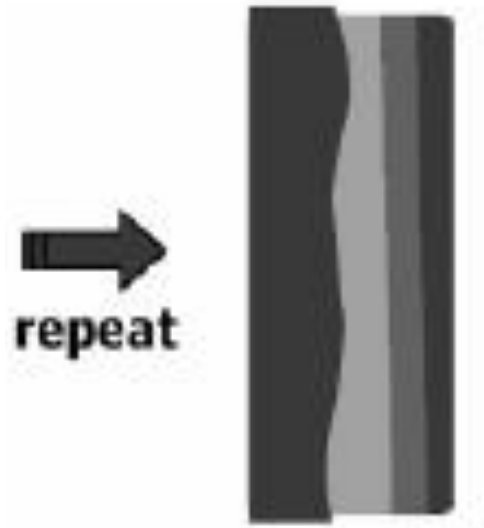
Water Hydrolysis

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

Surface Sol-Gel Processing



Resorption of Metal Alkoxide

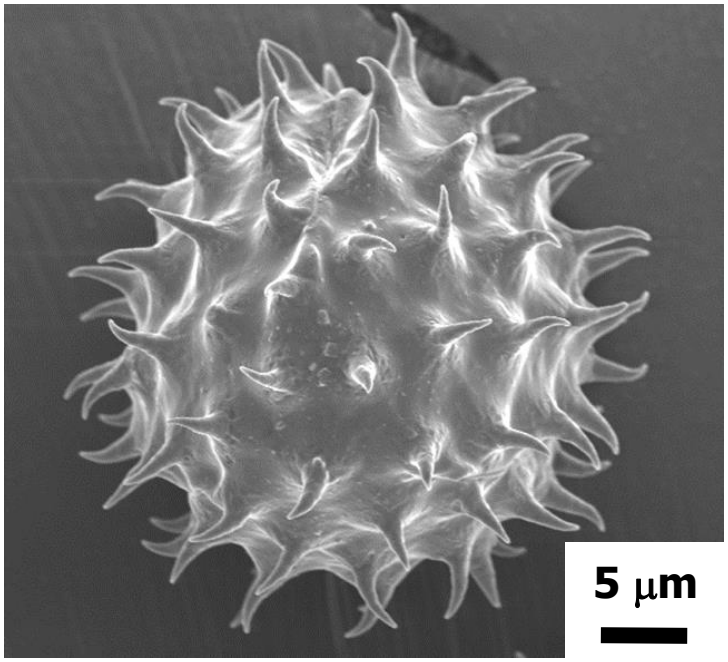


Layering of Ultrathin Metal Oxide

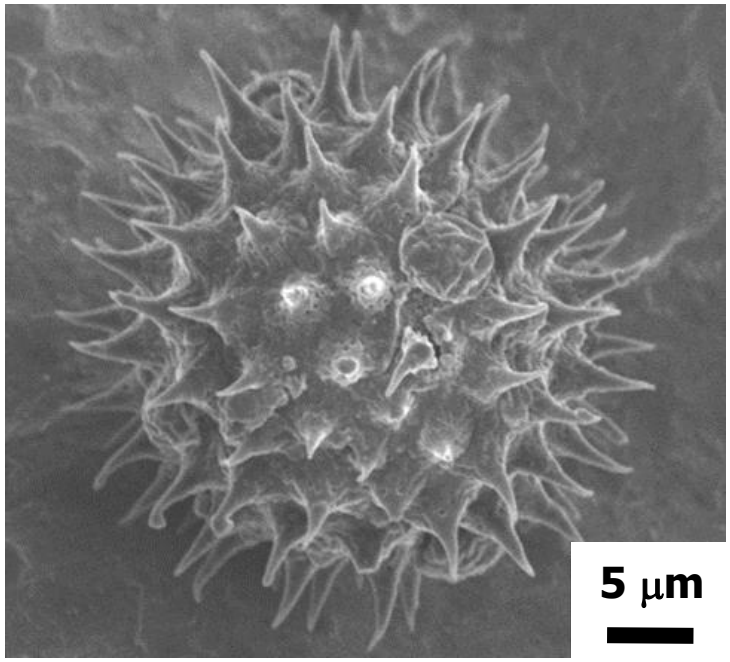
(obtained from S. Fujikawa, R. Takaki, T. Kunitake, *Langmuir*, 21, 8899 (2005))

Conformal Fe-O Coating of Sunflower Pollen

Native Sunflower Pollen



Fe-O Coated Pollen



Secondary electron images

(30 SSG cycles with Fe(III) isopropoxide)

I. J. Gomez, et al., *J. Mater. Chem.*, 3, 632 (2015);
W. B. Goodwin, et al., *Chem. Mater.*, 25, 4529 (2013)

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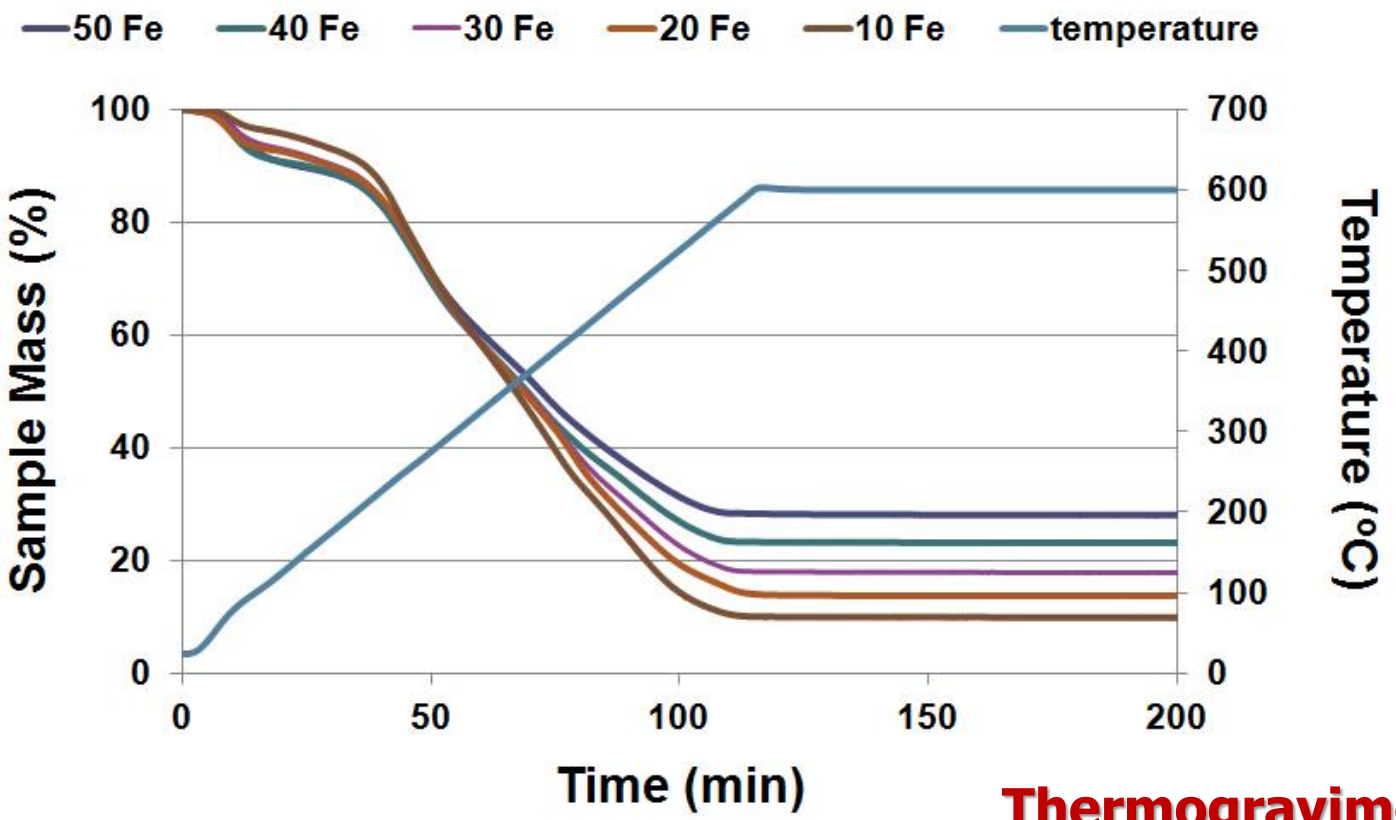
Organic Pyrolysis



Thermogravimetric Analyses

(5°C/min to 600°C in air)

I. J. Gomez, et al., *J. Mater. Chem.*, 3, 632 (2015)

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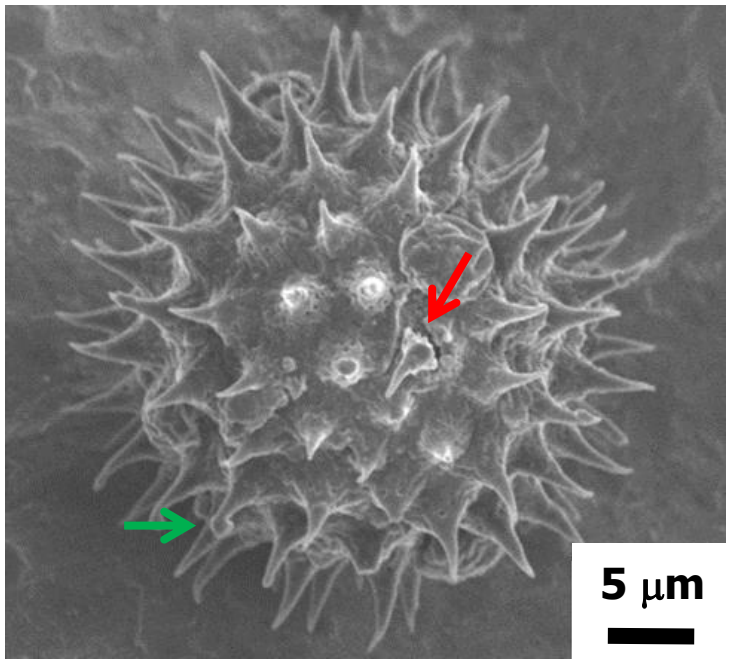
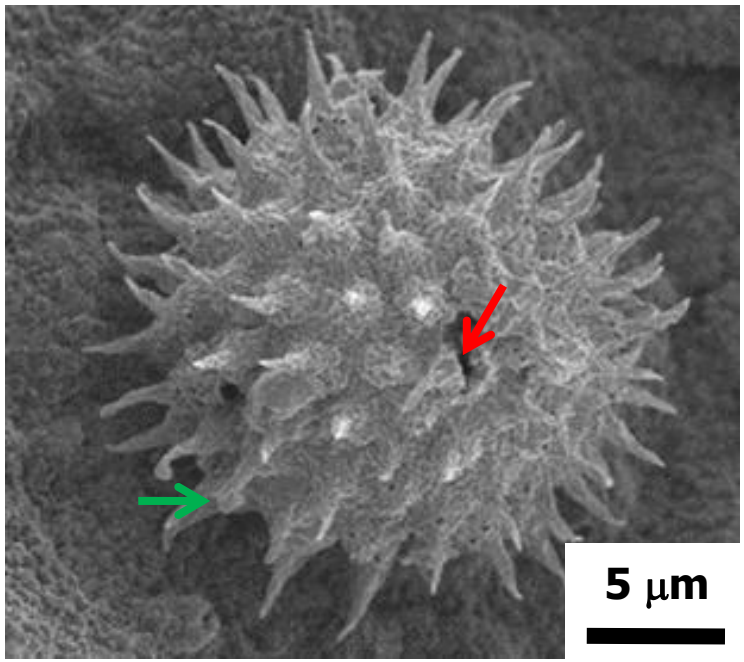
Iron Oxide Sunflower Pollen Replicas

Fe-O Coated Pollen



Fe_3O_4 Pollen Replica



Secondary electron images

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

I. J. Gomez, et al., *J. Mater. Chem.*, 3, 632 (2015);
W. B. Goodwin, et al., *Chem. Mater.*, 25, 4529 (2013)

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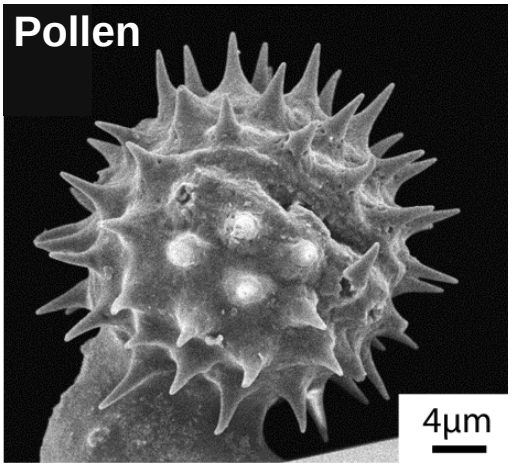
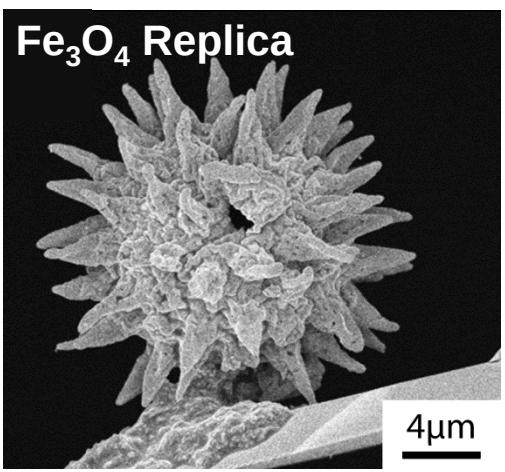
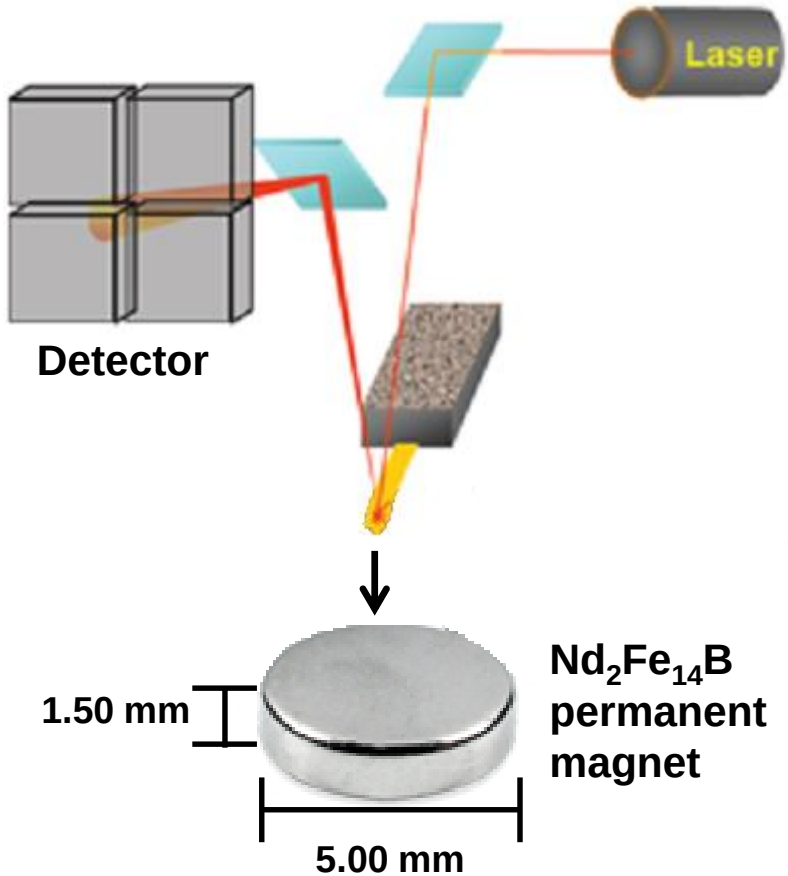
Adhesion Testing of Pollen and Pollen Replicas







I. J. Gomez, et al., *J. Mater. Chem.*, 3, 632 (2015)

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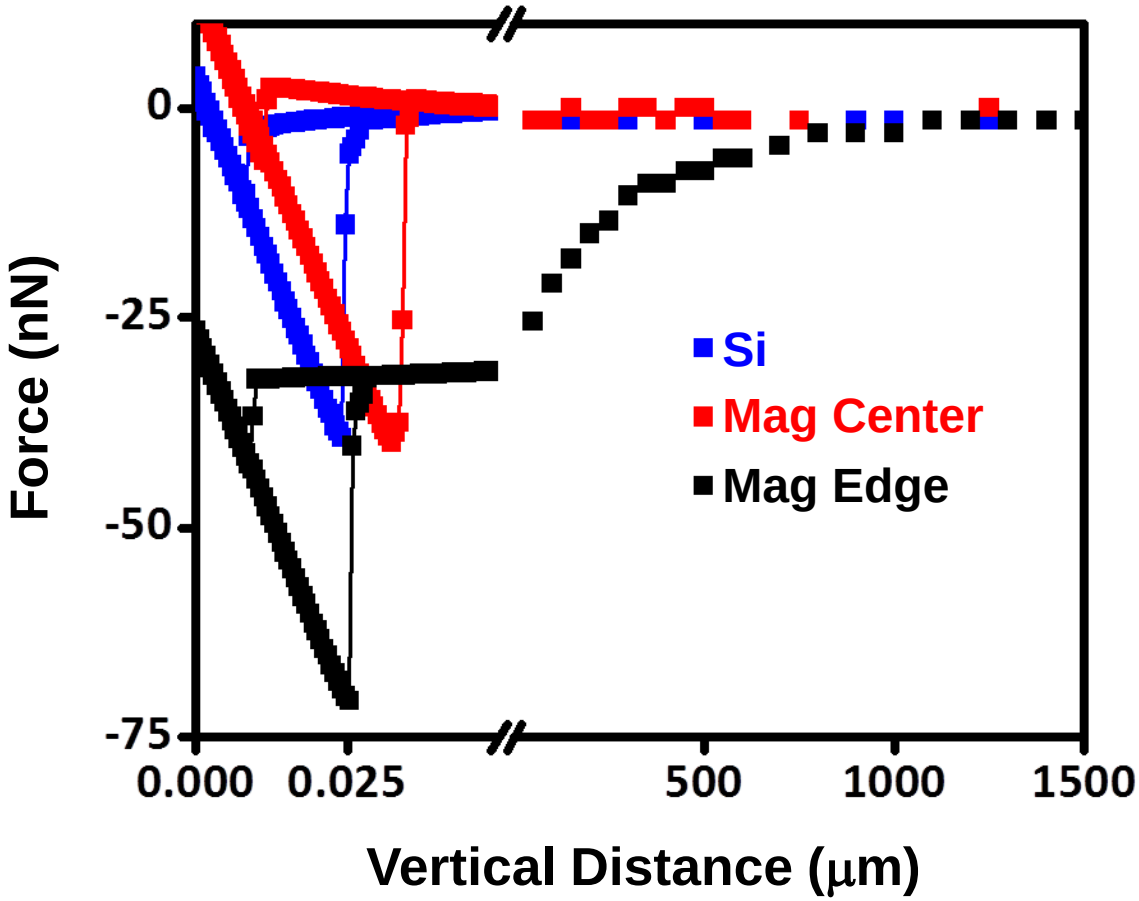
Multi-modal Adhesion of Fe_3O_4 Replicas



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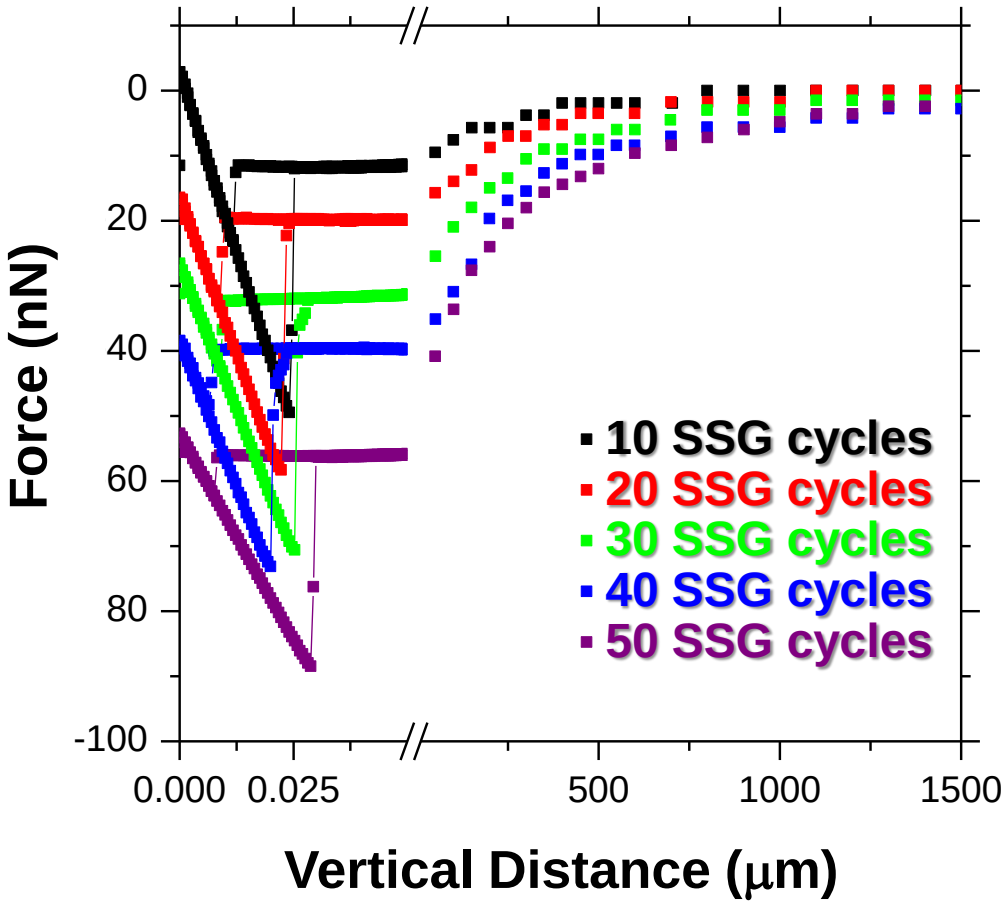
Tailorable Long Range Magnetic Adhesion



I. J. Gomez, et al., *J. Mater. Chem.*, 3, 632 (2015)

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Papilio blumei Butterfly

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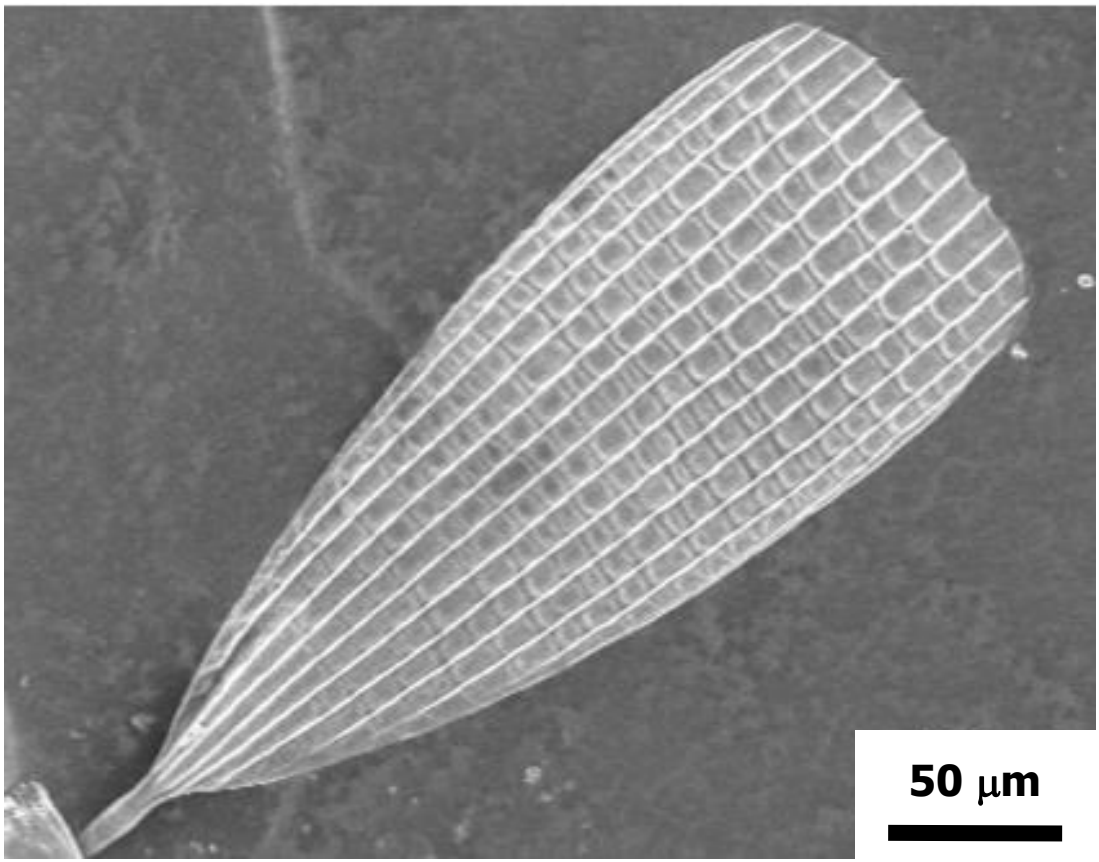
Green Ventral Scale of P. blumei Butterfly



Secondary electron image

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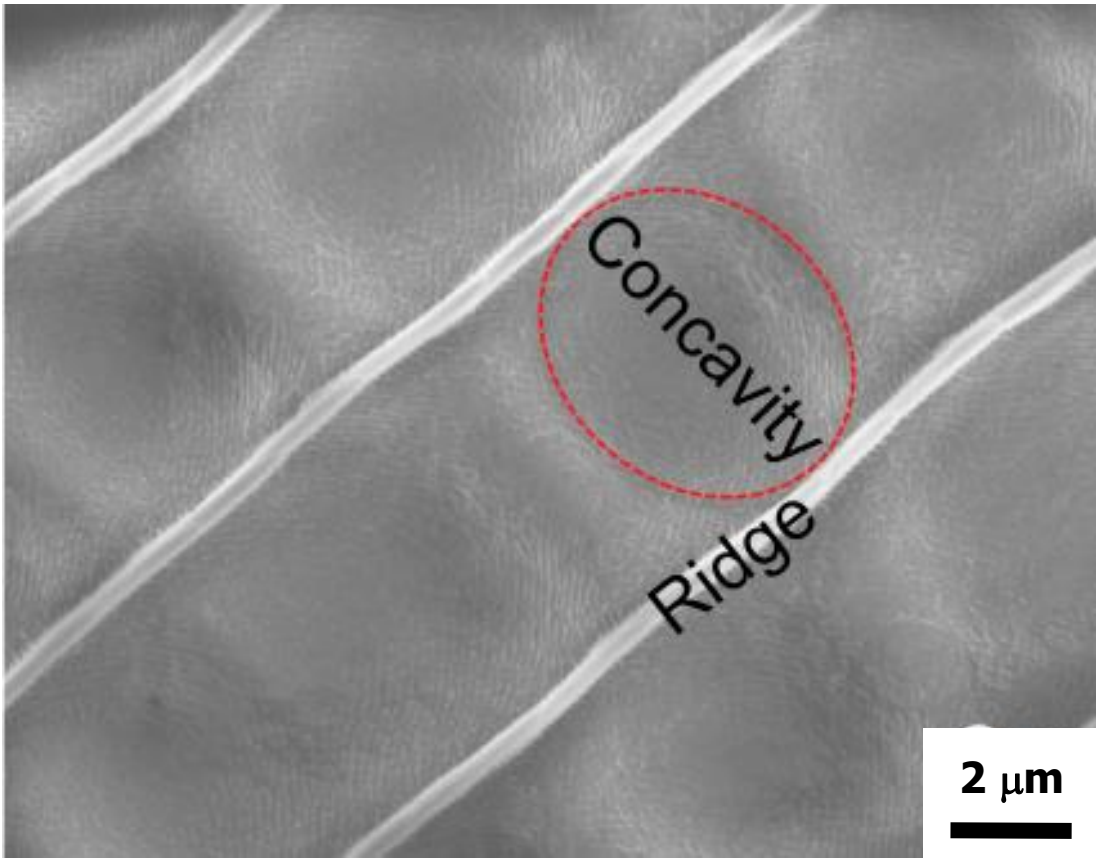
Green Ventral Scale of P. blumei Butterfly



Secondary electron image

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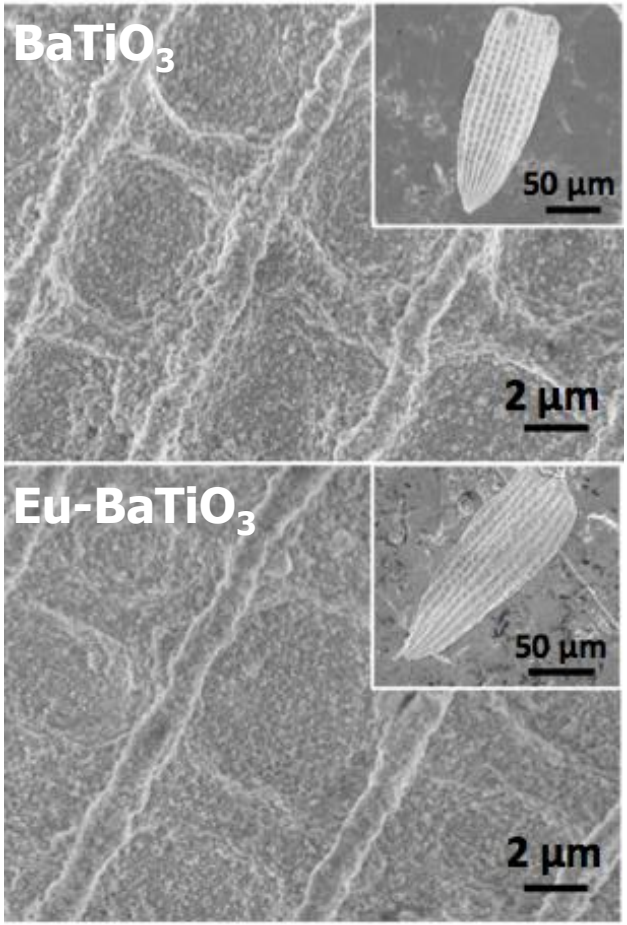
Eu-doped $BaTiO_3$ Replicas of P. blumei Scales

Secondary electron images



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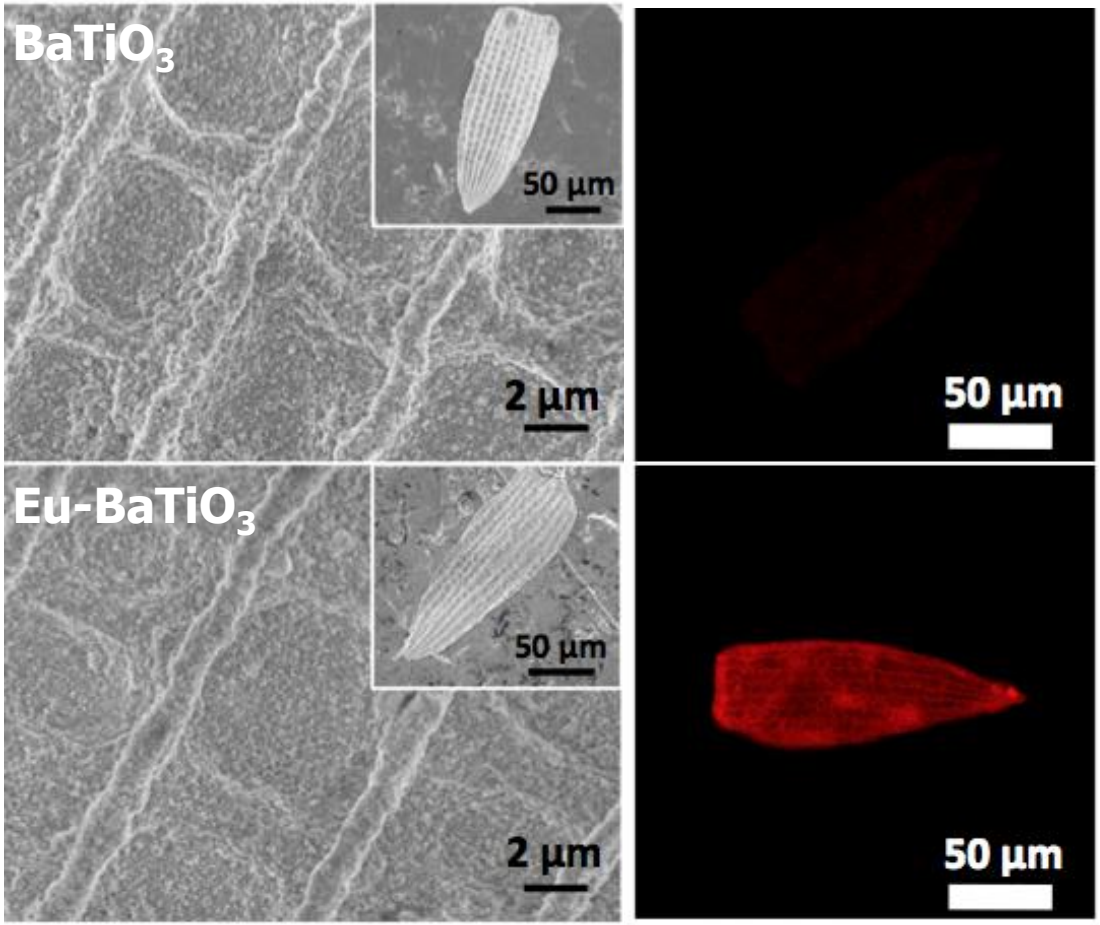
Eu-doped $BaTiO_3$ Replicas of P. blumei Scales

Secondary electron images



488 nm excitation, >585 nm emission

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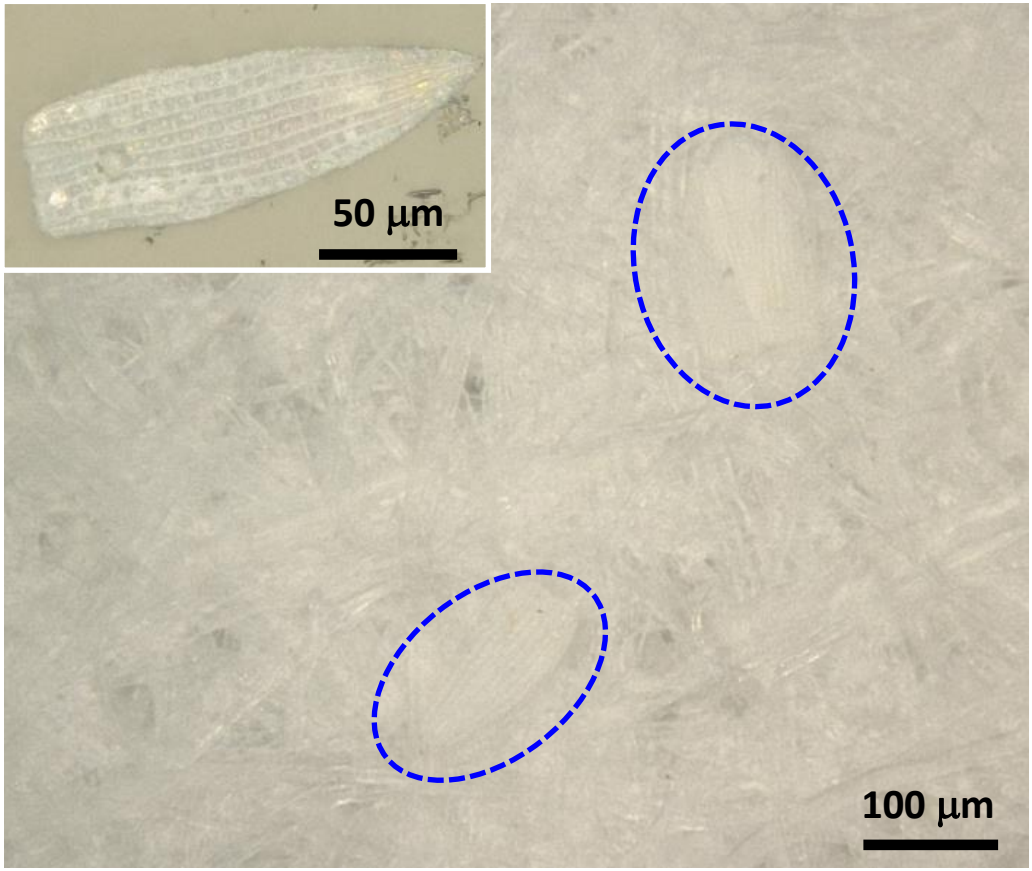
Labeling with Eu-$BaTiO_3$ P. blumei Replicas



Bright field image

(Eu-$BaTiO_3$ replica scales on cellulose filter paper)

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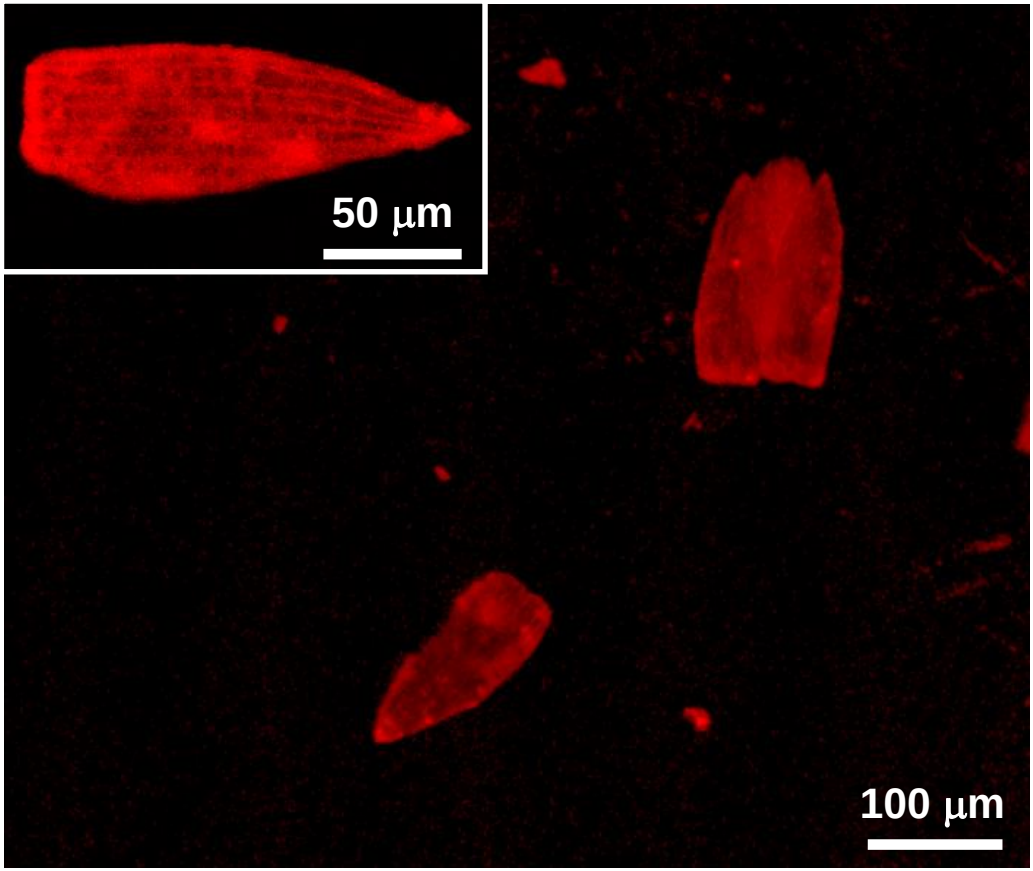
Labeling with Eu-$BaTiO_3$ P. blumei Replicas



Fluorescence image

(Eu-$BaTiO_3$ replica scales on cellulose filter paper)

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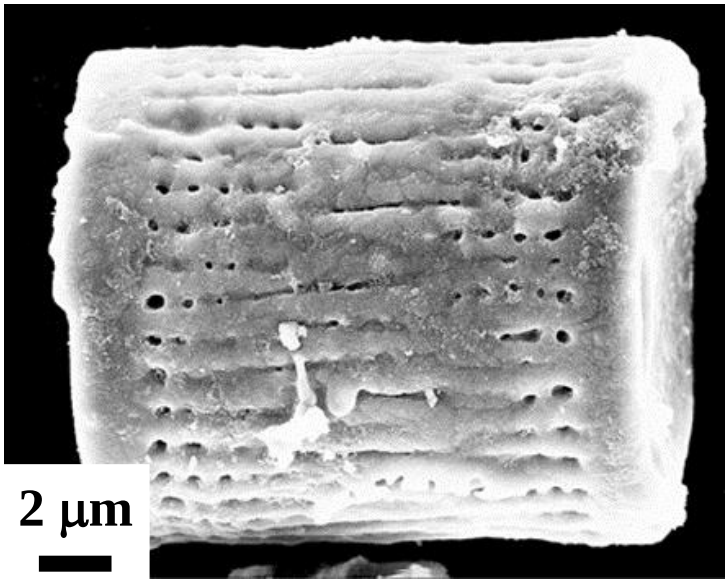
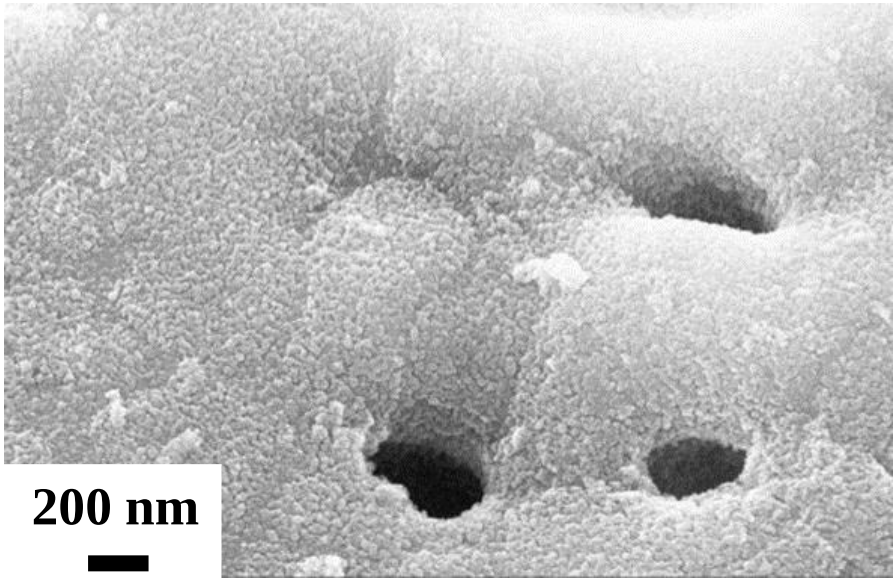
Fe_3O_4-coated Frustules





Secondary electron images

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

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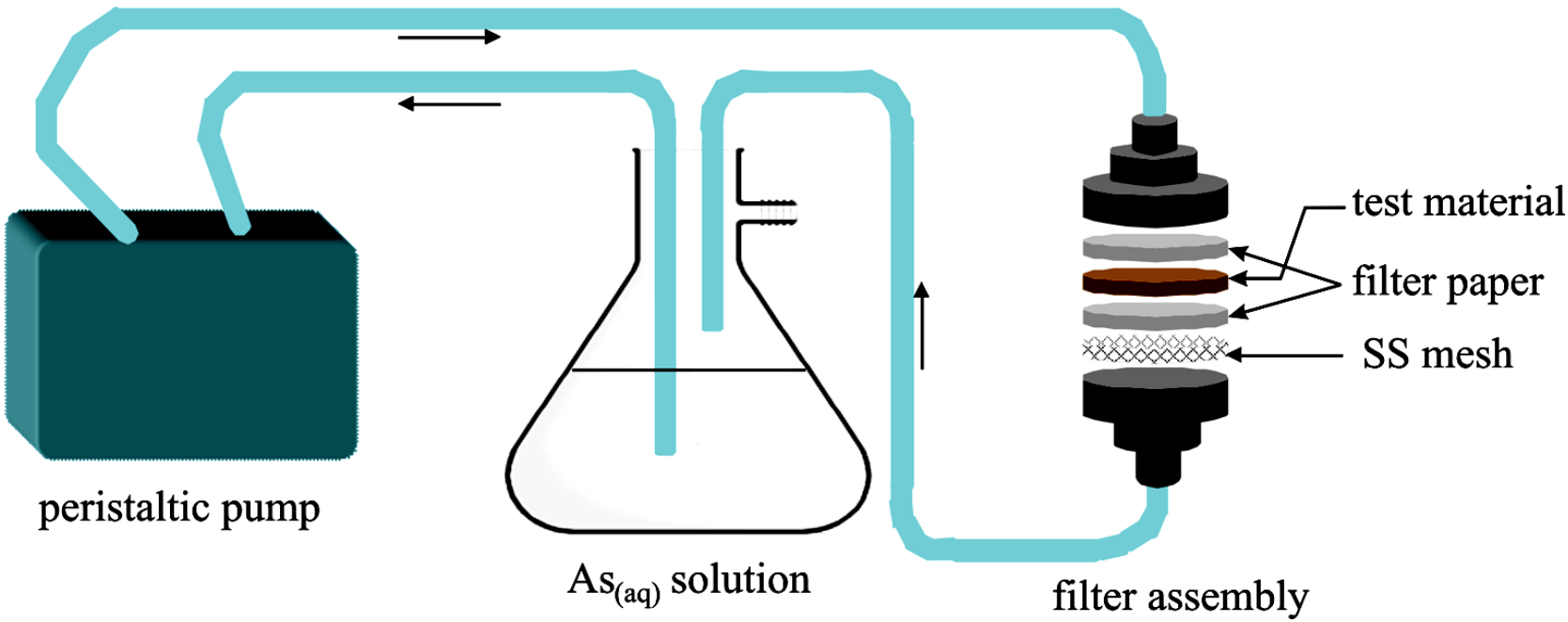
As Adsorption Experiments



	SSA (m^2/g)	Porosity (vol%)
Commercial Fe_3O_4 (CM):	44.0	68
Fe_3O_4 Diatoms (MD):	4.7	55

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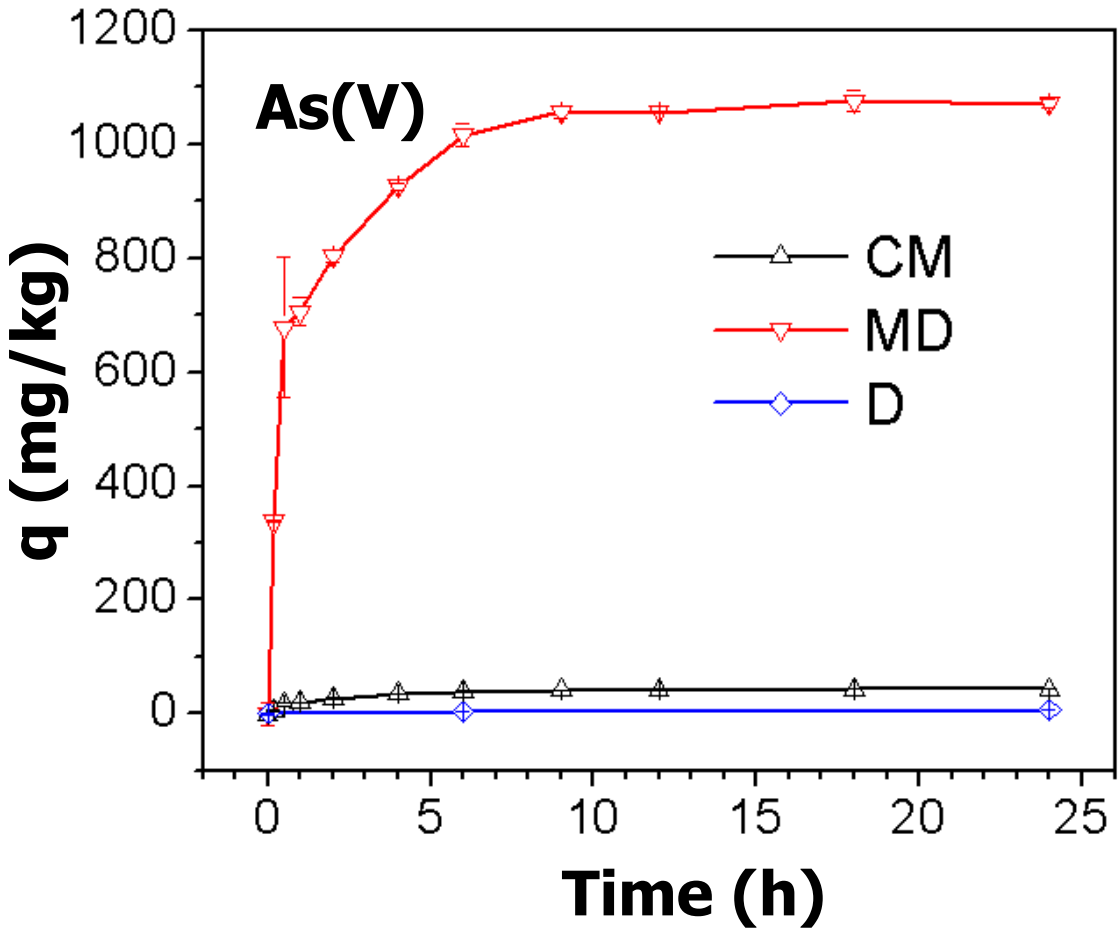
As Removal from Water w/Fe_3O_4-coated Frustules



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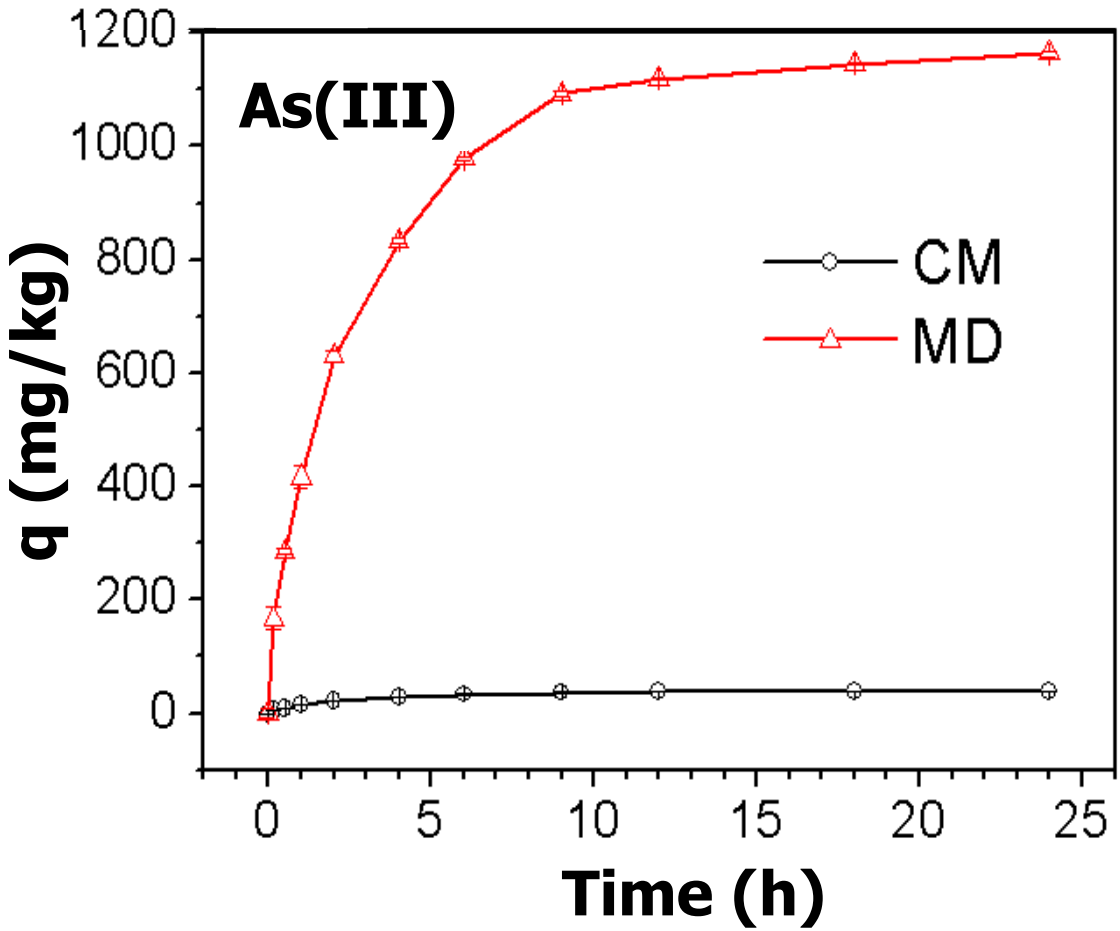

	SSA (m^2/g)	Porosity (vol%)
CM:	44.0	68
MD:	4.7	55

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Summary

- ***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_3O_4, SnO_2, TiO_2, ZrO_2, $BaTiO_3$, Eu-$BaTiO_3$)**

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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_3O_4 pollen replicas)
- **Optical micromarkers**
  - Shaped photoluminescent particles (Eu-$BaTiO_3$ butterfly scales)
- **Water (and other fluid) purification**
  - Arsenic adsorption (Fe_3O_4-coated diatom frustule replicas)

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Acknowledgements

The financial support of the:

- **U.S. AFOSR/AFRL: BIONIC Center of Excellence (Bio-nano-enabled Inorganic/Organic Nanocomposites and Improved Cognition)**
- **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)**

are gratefully acknowledged.

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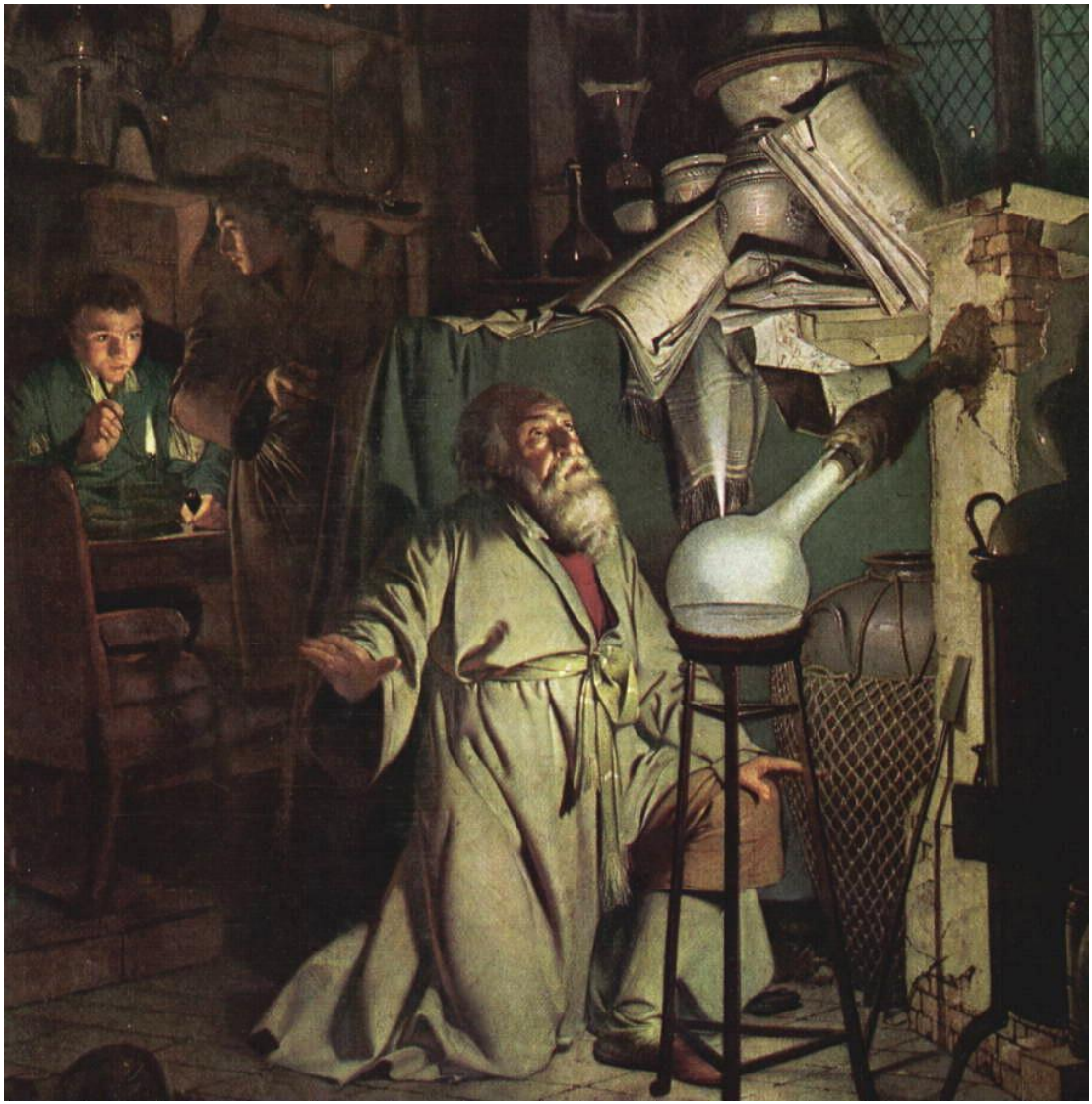
Biomaterials Alchemy: Questions? Suggestions?



***The Alchymist*,**
Joseph Wright, 1771