From Bioinspired to Bioinformed Design of Sustainable Materials

Engineered Living Materials

Matteo Hirsch

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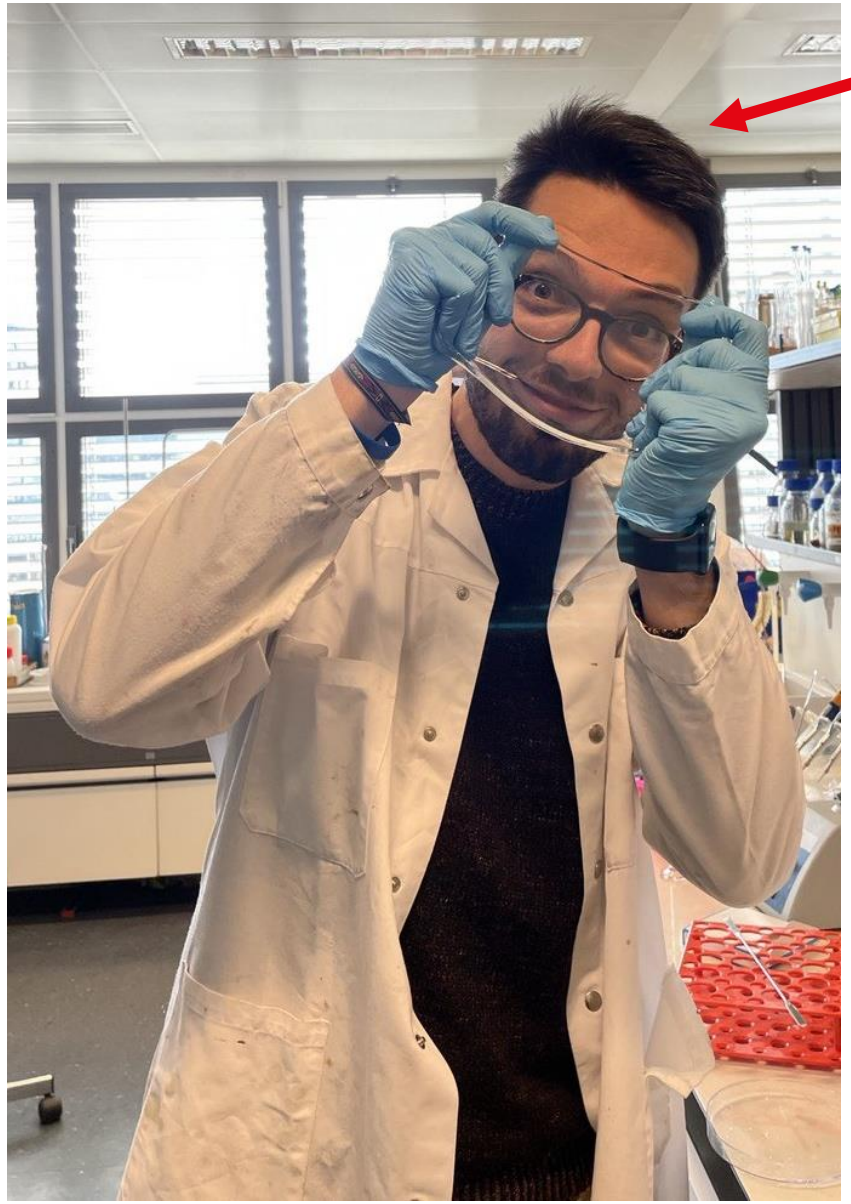
24th September 2024

About Me



Matteo, 30-year-old Postdoc from Florence (IT)

B. Sc. in **Biomedical Engineering** at Polytechnic of Turin (IT)

- Biomechanics, Biomaterials, Medical Devices

M. Sc. in **Nanotechnologies** at Polytechnic of Turin (IT), Grenoble (FR), and EPFL (CH)

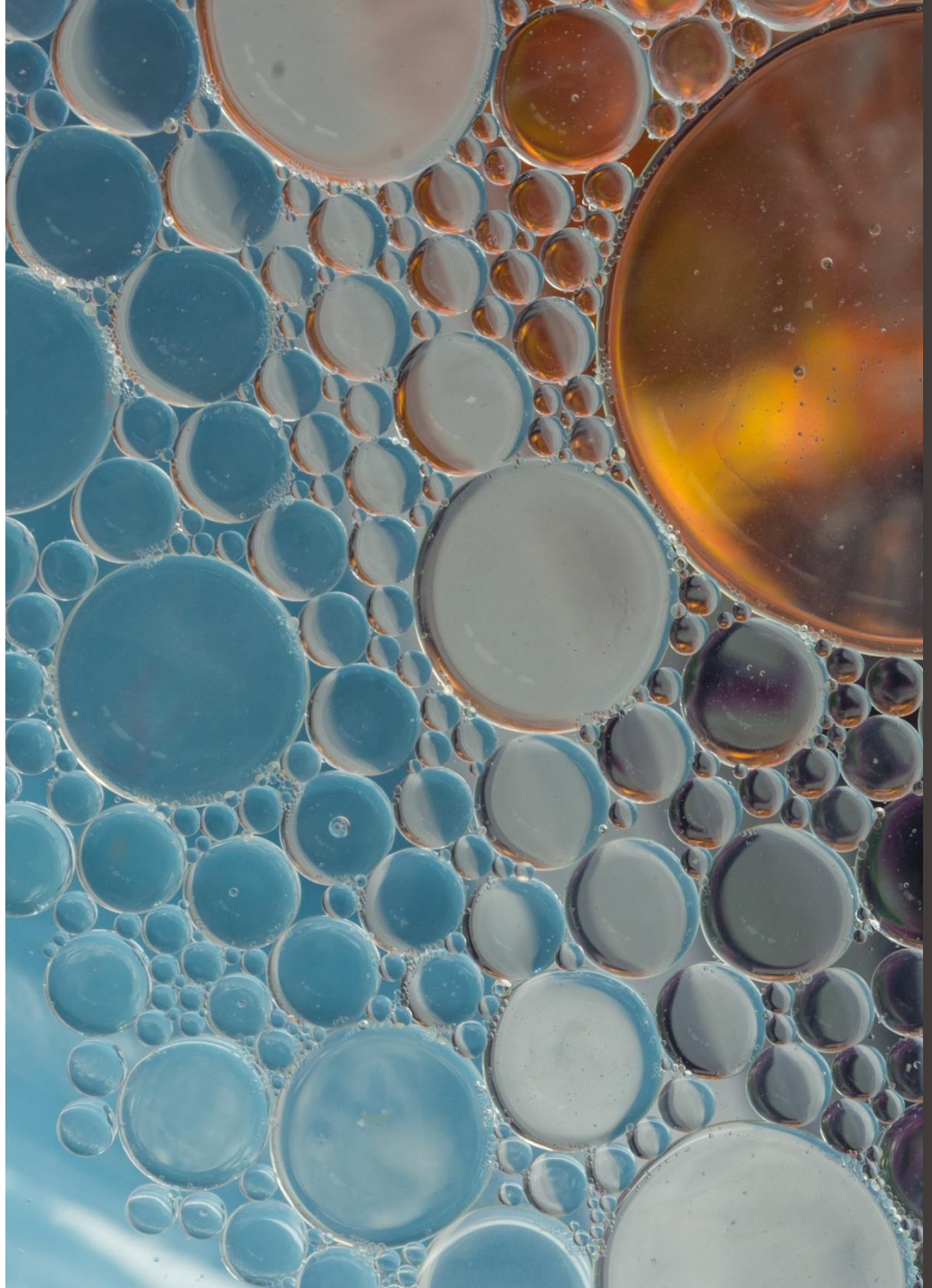
- Electronics, Nanomaterials, Nanomedicine

Research Experience

- LMU München (Germany)
- Houston Methodist Research Institute (Houston, TX)

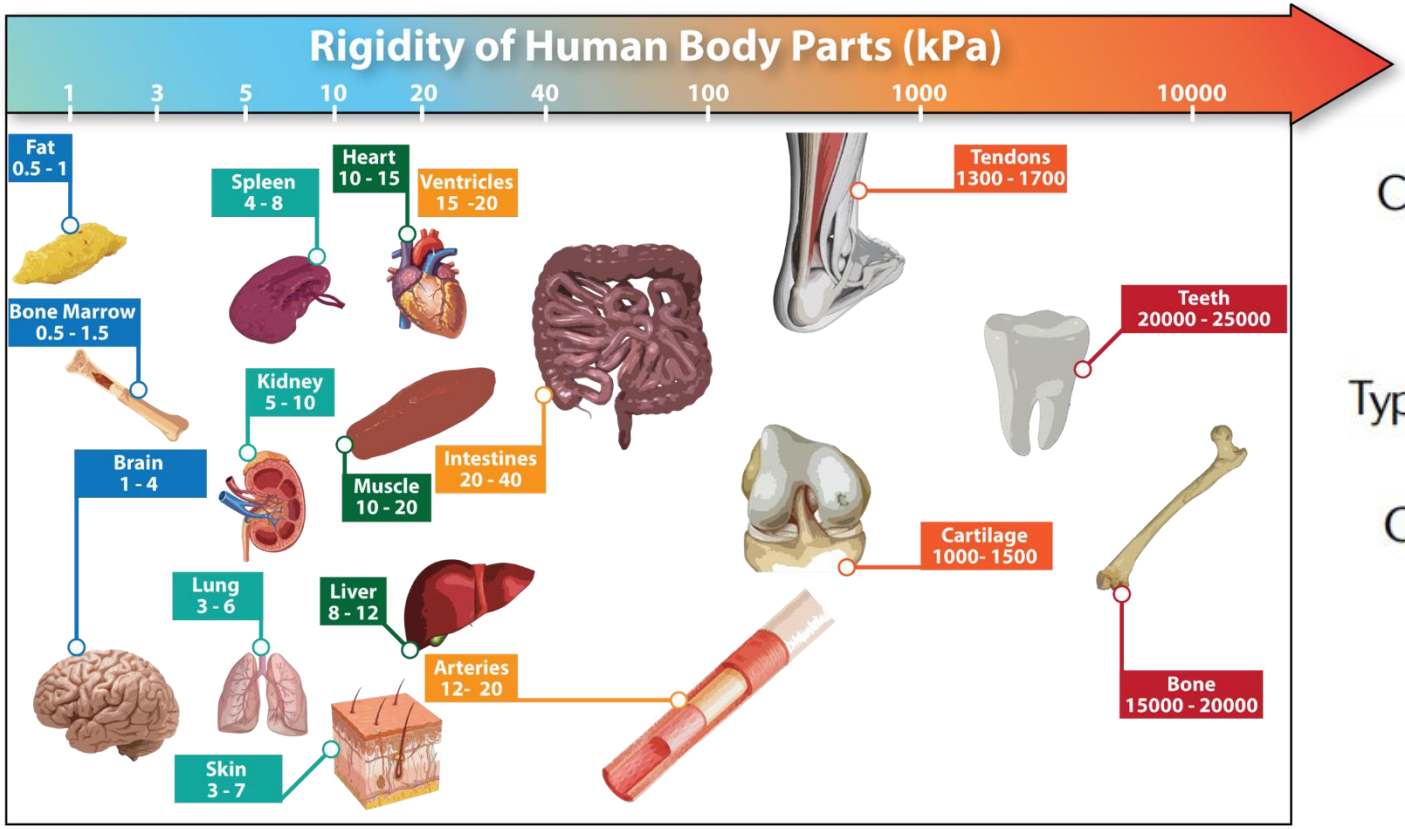
PhD and **Postdoc** in **Materials Science** at EPFL

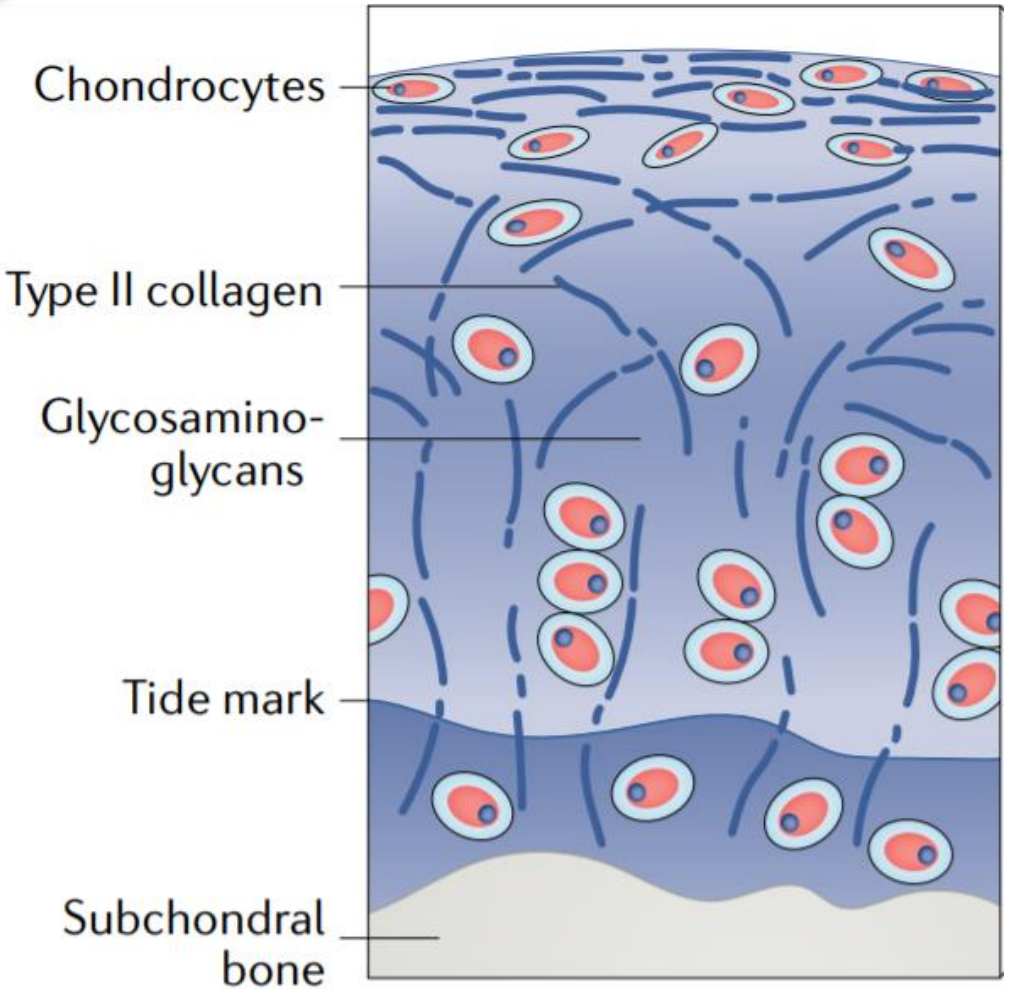
- Soft Materials, 3D Printing, Sustainable Materials, Engineered Living Materials



Introduction

The Ideal Material in Tissue Engineering





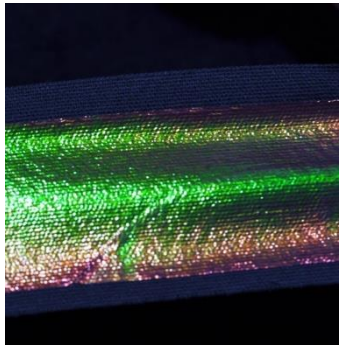
The material design should account for both mechanical and structural requirements

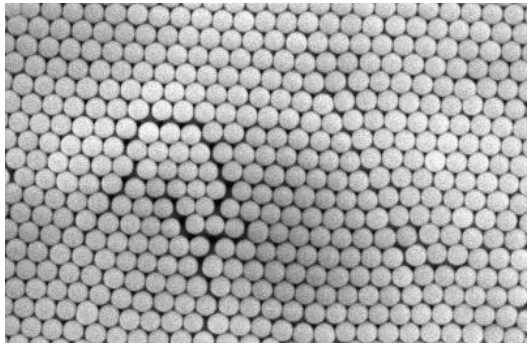
Courtesy of Prof. Xuanhe Zhao, MIT (USA)

Kwon, H. *et al., Nature Reviews Rheumatology,* (2019)

Bioinspiration vs Bioinformation

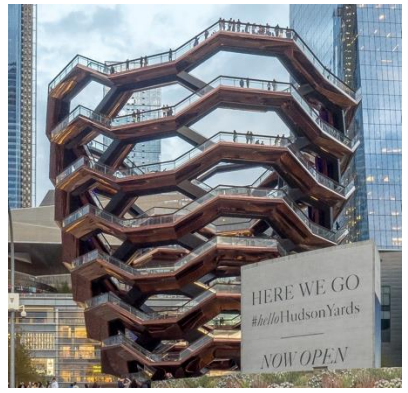
Bioinspiration





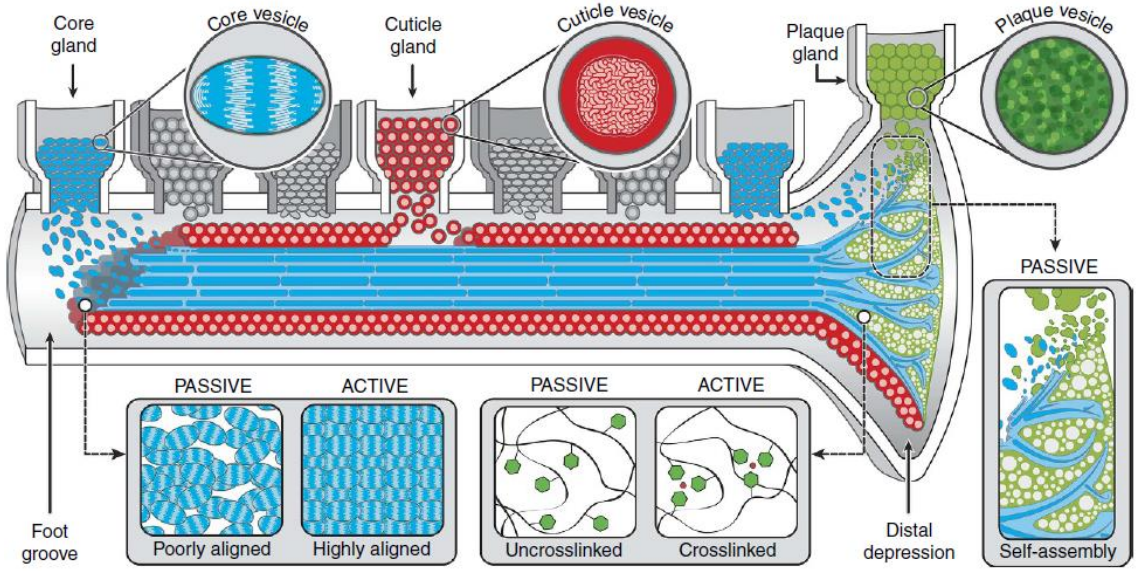
- Higher degree of complexity
- Technology-limited

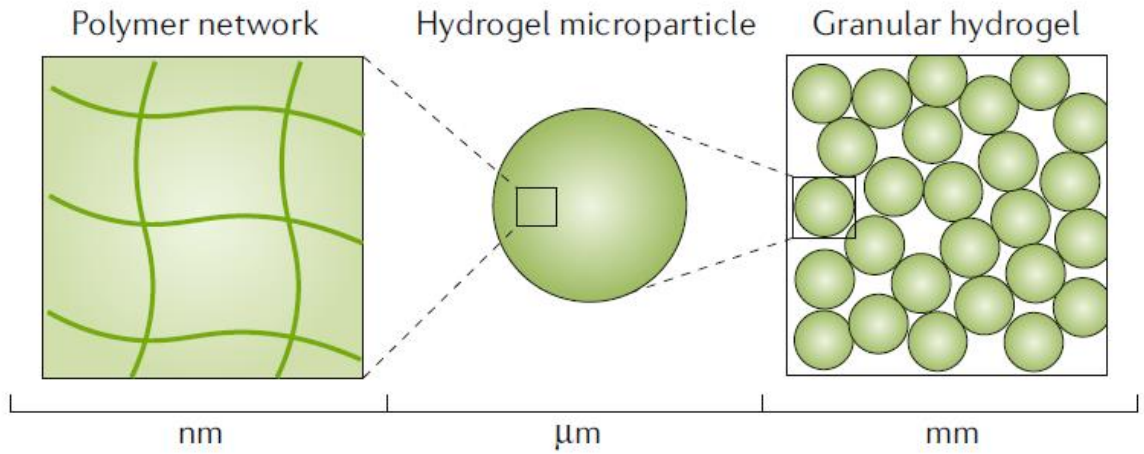
Bioinformation



- Easier implementation
- Versatile

A Lesson from Nature





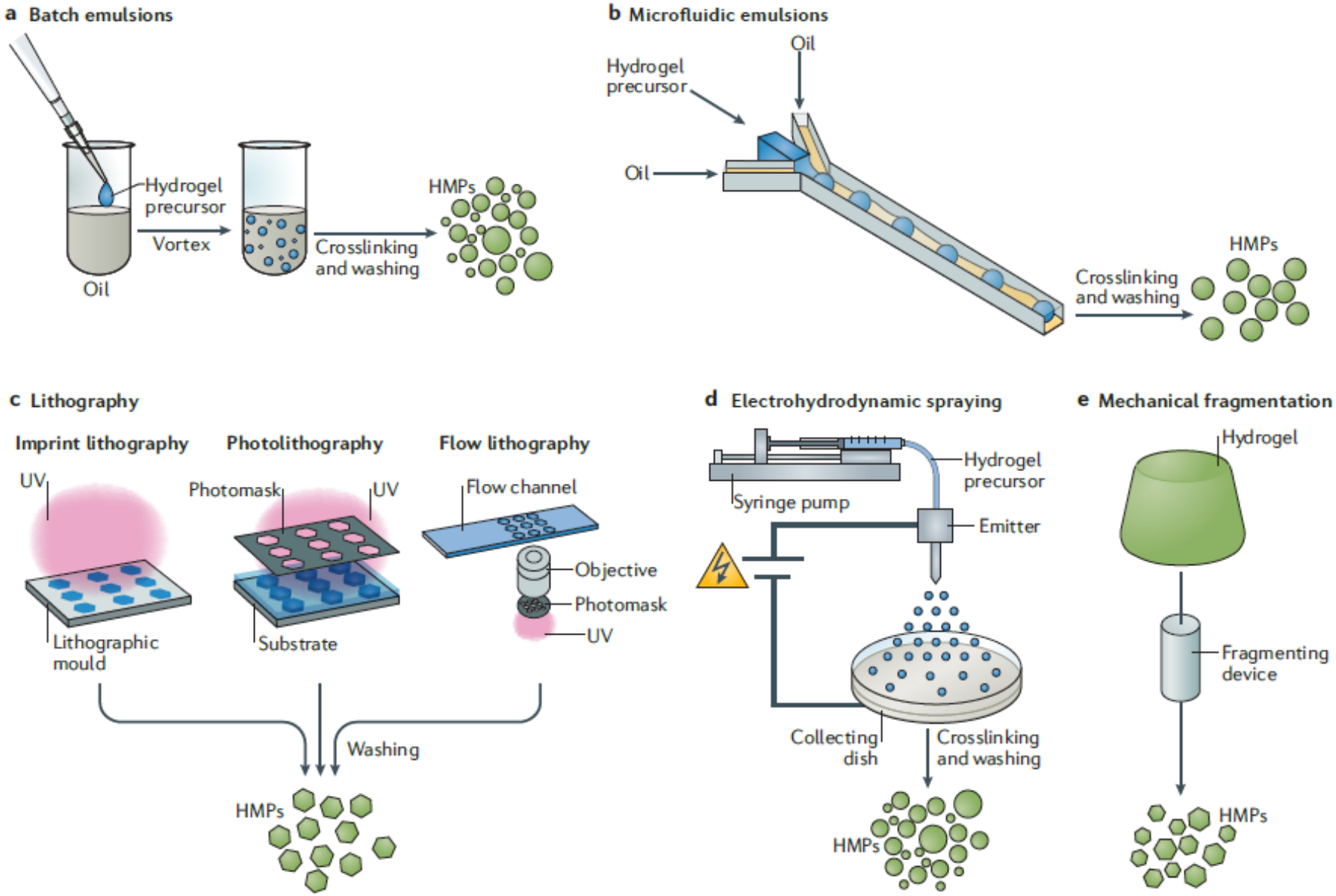
Priemel, T. *et al.. Nature Communication*, 8, 14539 (2017)

- Precursor-containing vesicles
- Transport and fast assembly
- Spatial heterogeneity

- Monomer-loaded drops
- Injectability and 3D printing
- Local varying composition

Adapted from: Daly, A. C. *et al.. Nature Reviews Materials,* (2019)

Hydrogel Microparticle Formation



Daly, A. C. *et al.. Nature Reviews Materials,* (2019)

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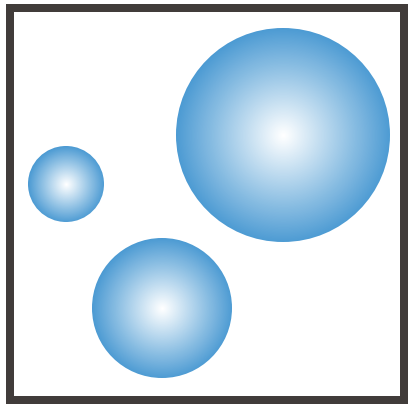
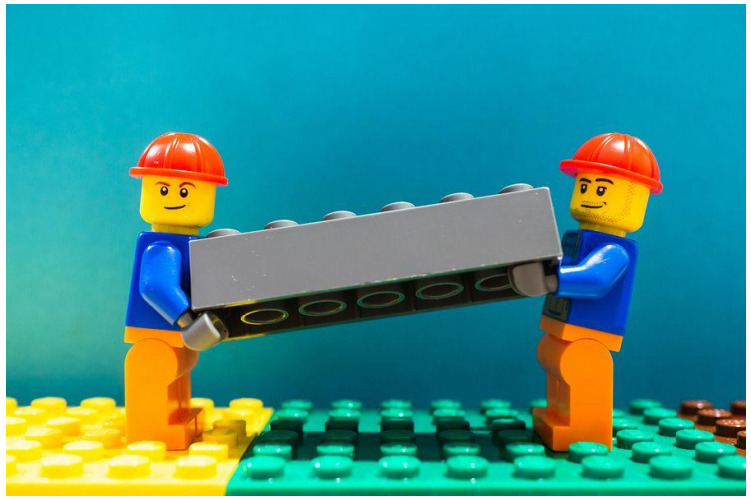
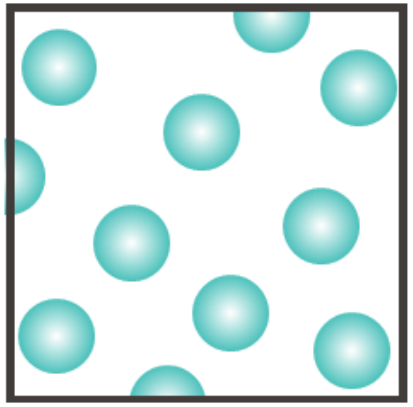
The Microgel Toolbox

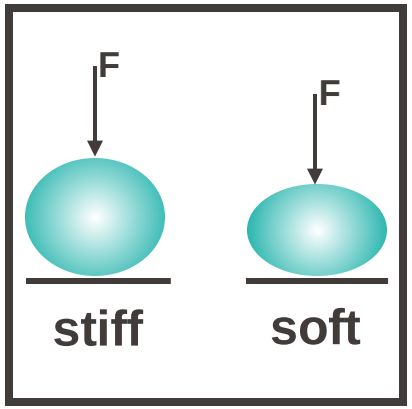


Size

- ✓ Polydispersity
- ✓ Shape

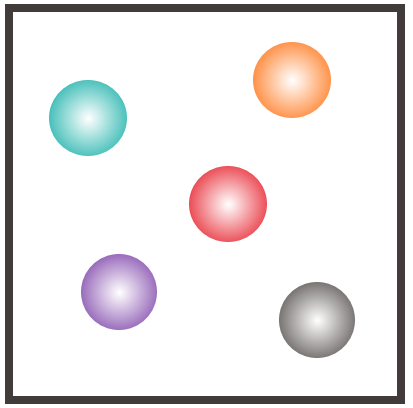






Stiffness

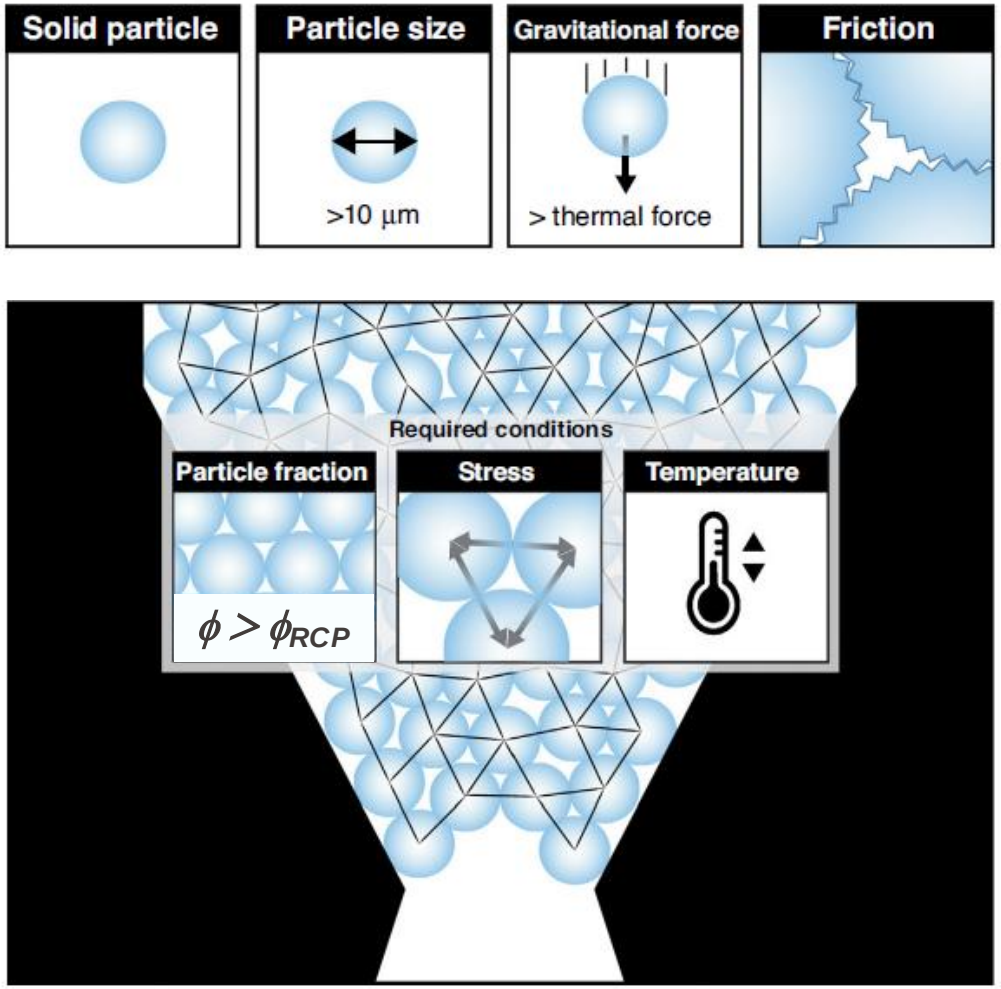
- ✓ Mechanics
- ✓ Packing



Composition

- ✓ Charge
- ✓ Responsiveness
- ✓ Swelling

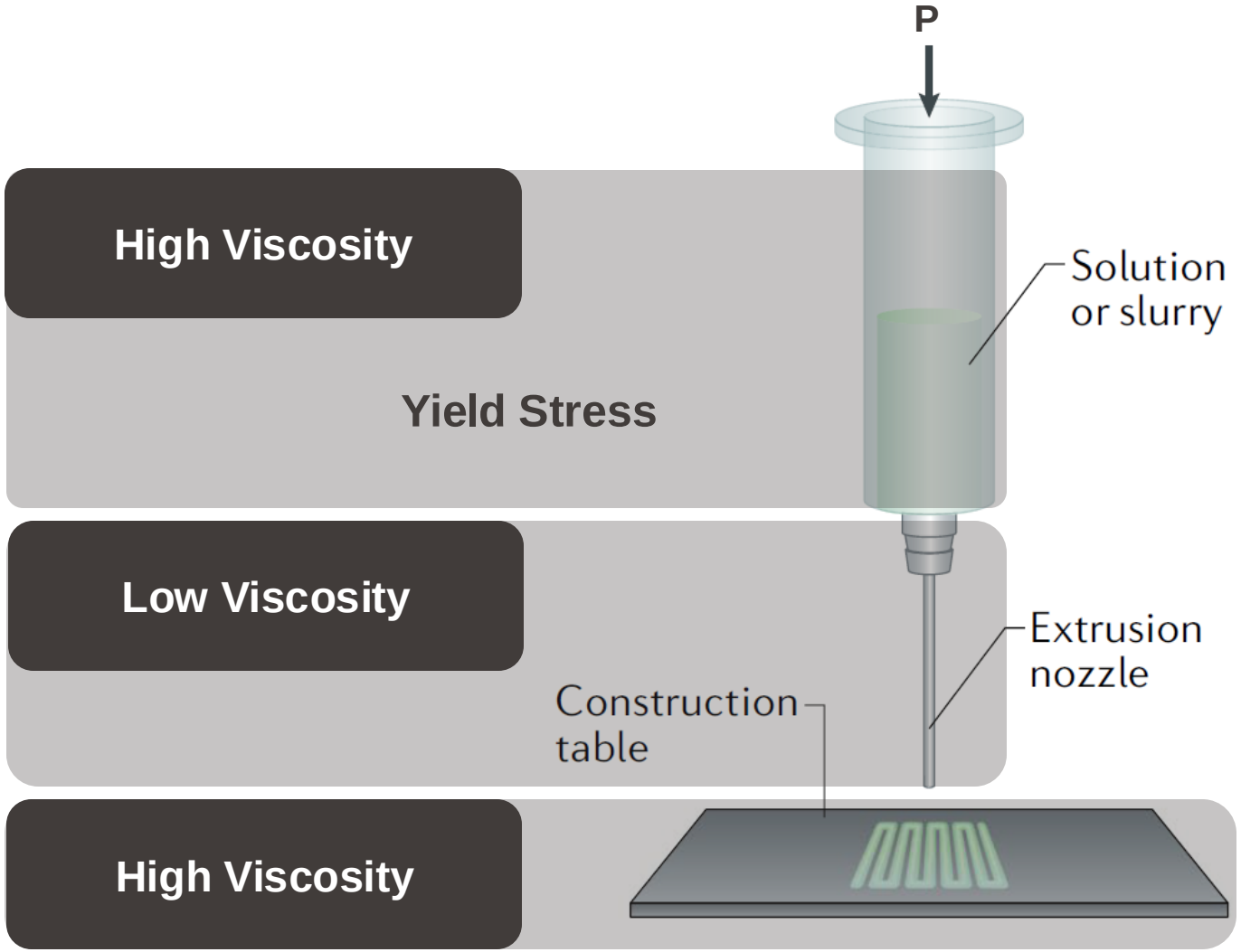
Jammed Microgels

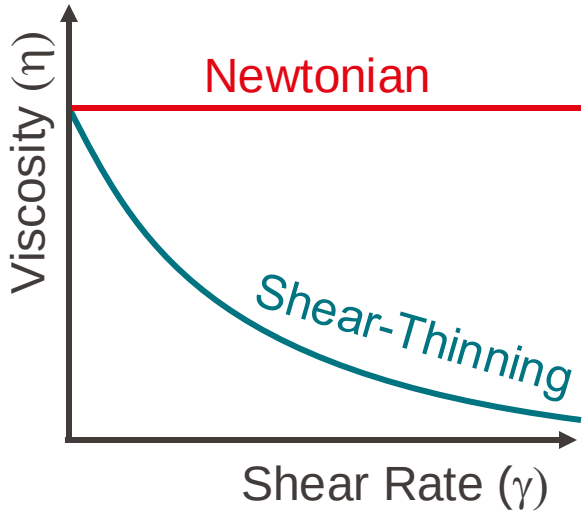


Jammed State – under specific temperature, stress, and density conditions the jammed material shows a transition from a liquid-like to a solid-like amorphous state

Adapted from: Riley, L. *et al.. Current Opinion in Biotechnology*, 60, 1-8 (2019)

3D Extrusion Printing





- Printability
- Shear recovery
- Print fidelity

Adapted from: Moroni, L. *et al. Nature Reviews Materials,* (2018)

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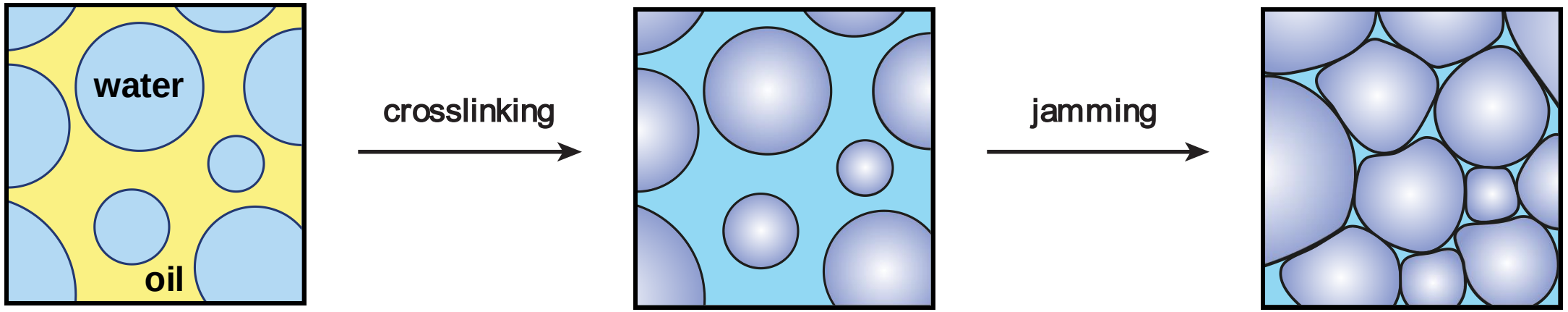
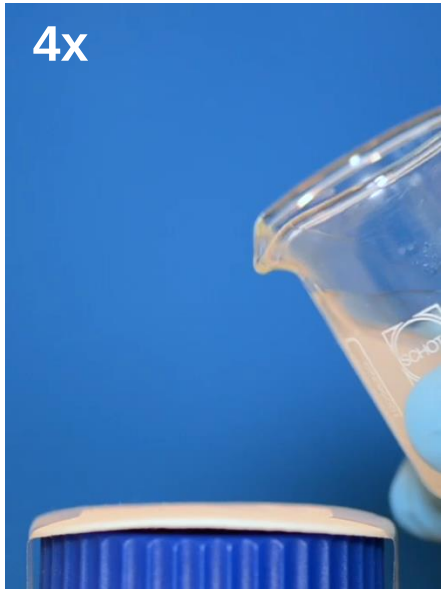
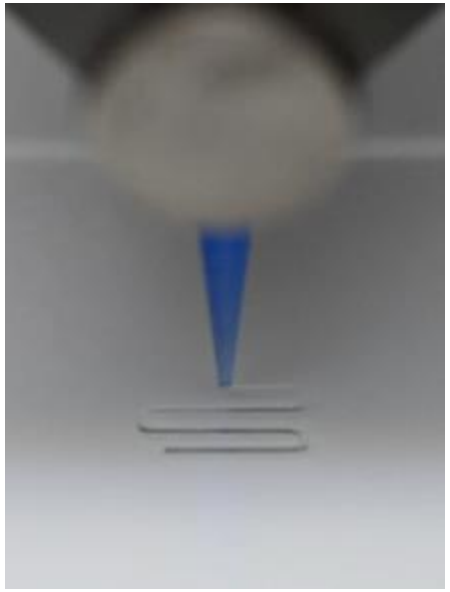
Jammed Microgel Synthesis







✓ Good printability
✓ High shape fidelity

X Lack of mechanical integrity

Adapted from: **Hirsch M.** *et al. Advanced Functional Materials.* 5, 2005929 (2021)

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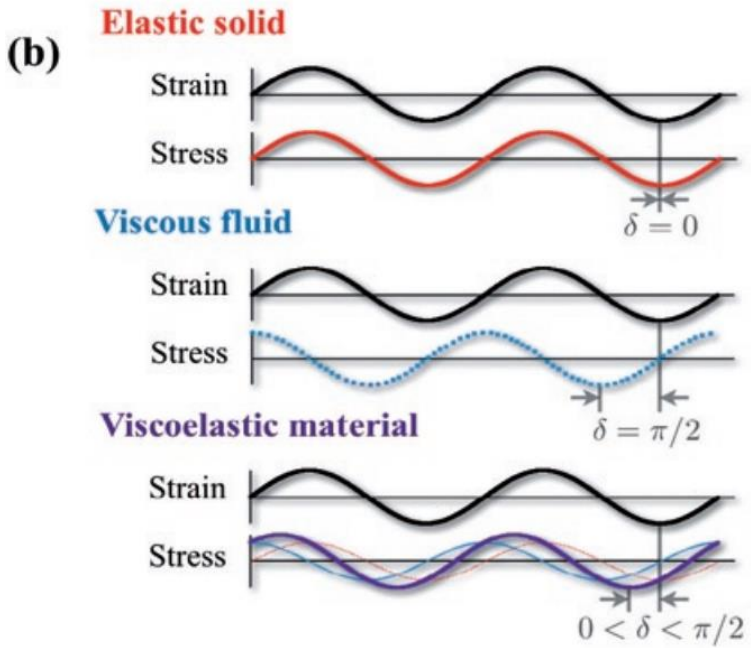
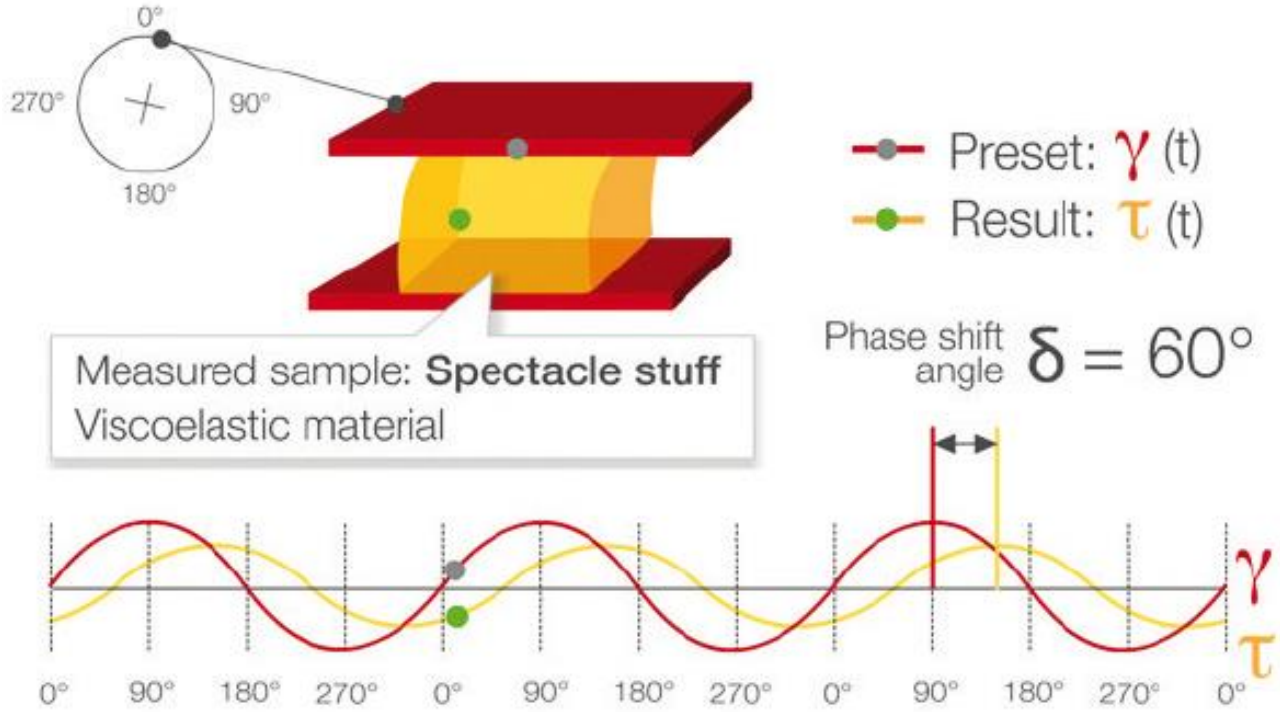
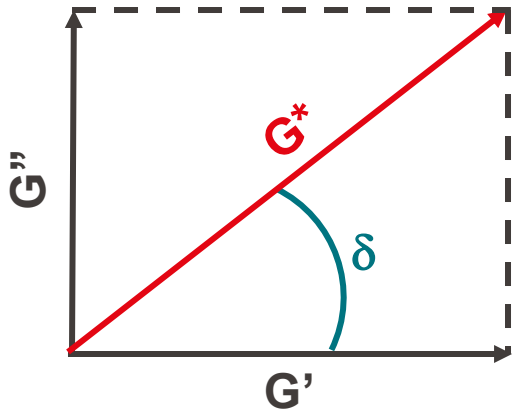
Rheology







$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$\sigma(t) = \sigma_0(\omega) \sin[\omega t + \delta(\omega)] = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)]$$

$$\tan\delta = G''/G' \text{ or } G^* = G' + iG''$$

Adapted from: Weitz, D. *et al. G.I.T. Laboratory Journal*, 3-4, 68-70 (2007)

Adapted from: https://wiki.anton-paar.com/en/basics-of-rheology/#c18437

Rheology of Jammed Microgels

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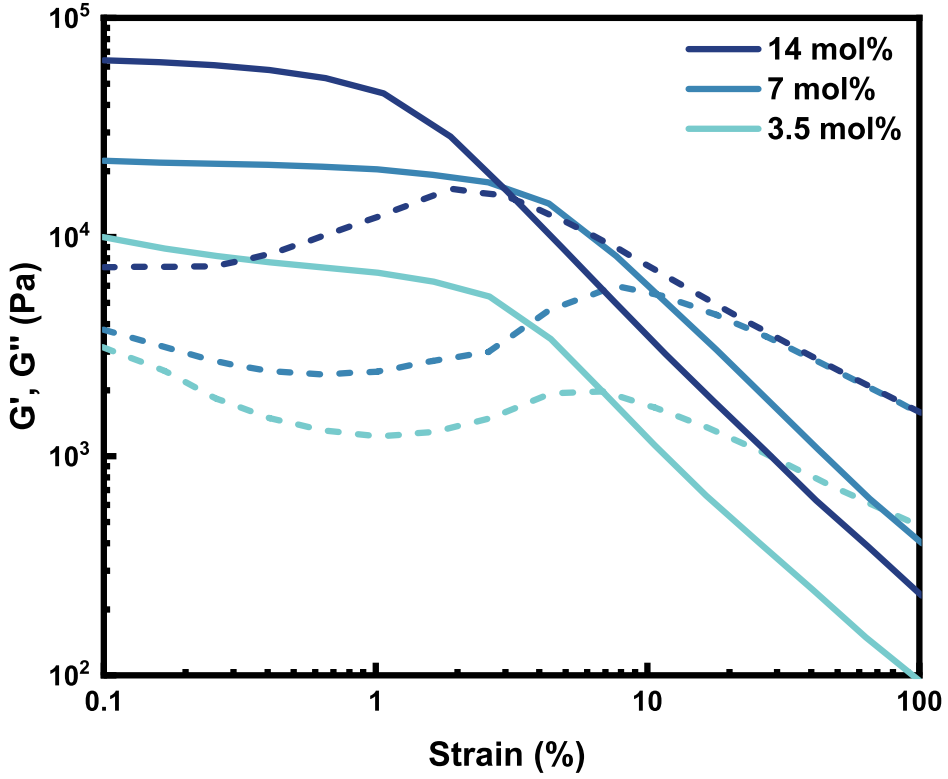
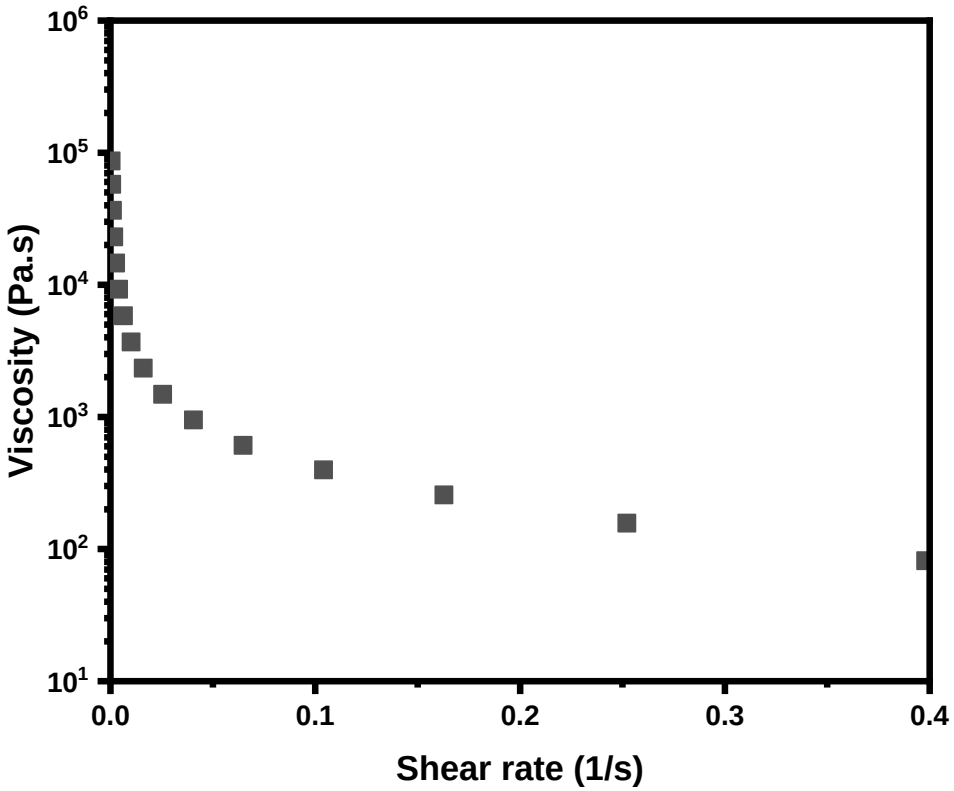
Yield Stress



Shear-thinning



G' > G'' solid-like – G'' > G' liquid-like

Hirsch M., Charlet A., and Amstad E. *Advanced Functional Materials*, 2005929 (2020)

Rheology of Jammed Microgels

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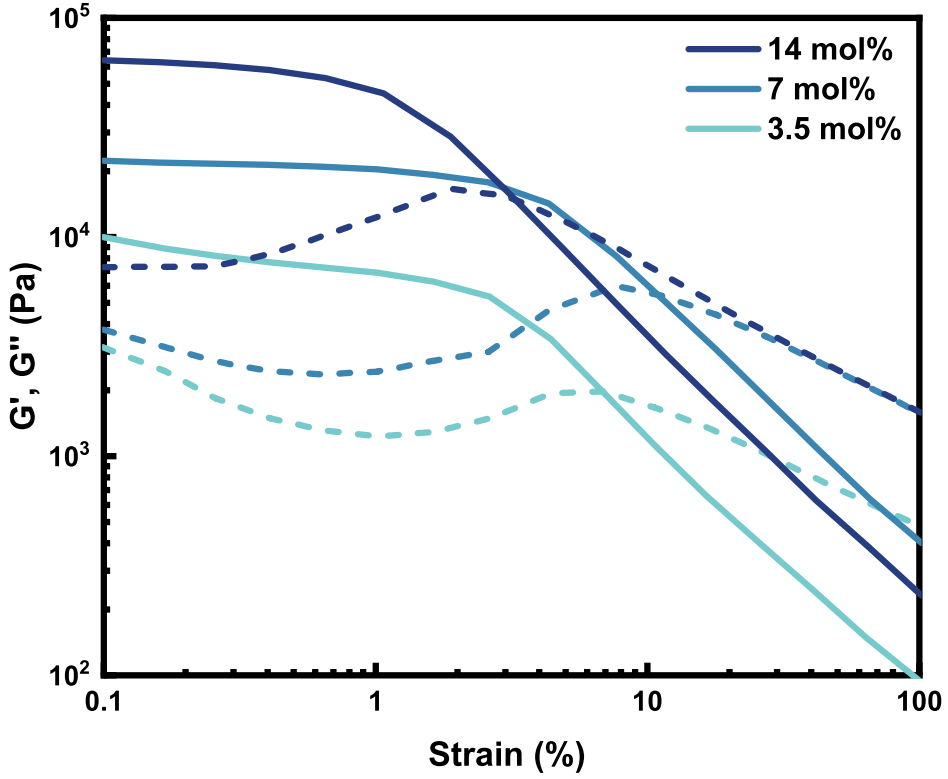
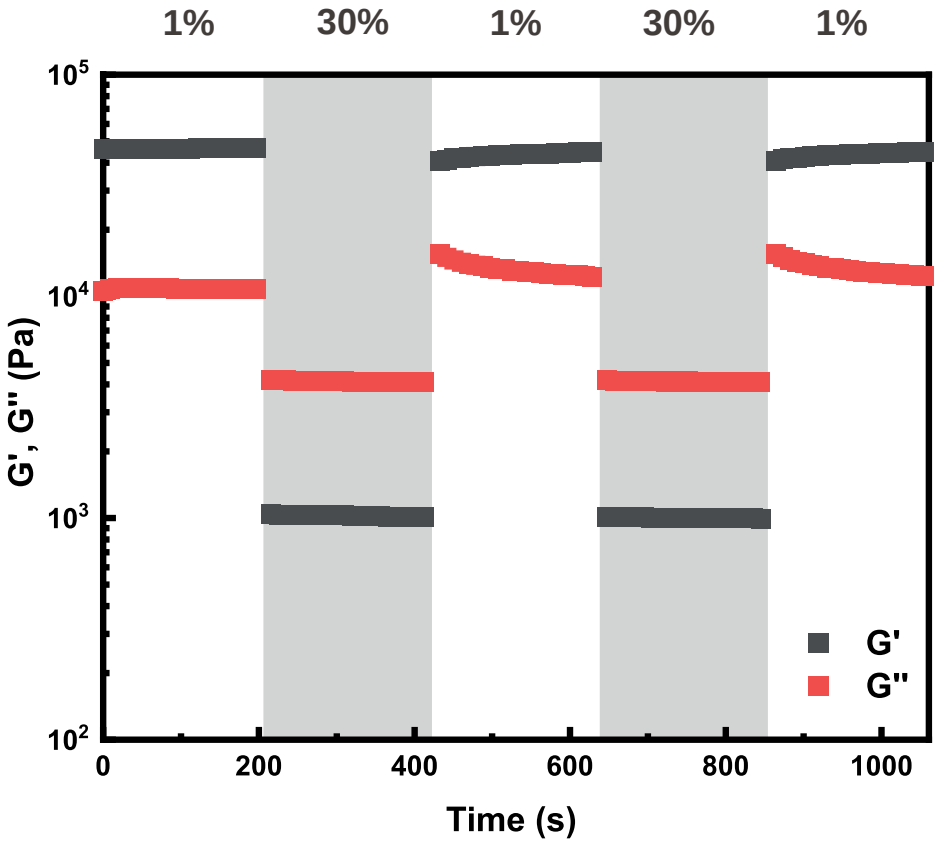
Yield Stress



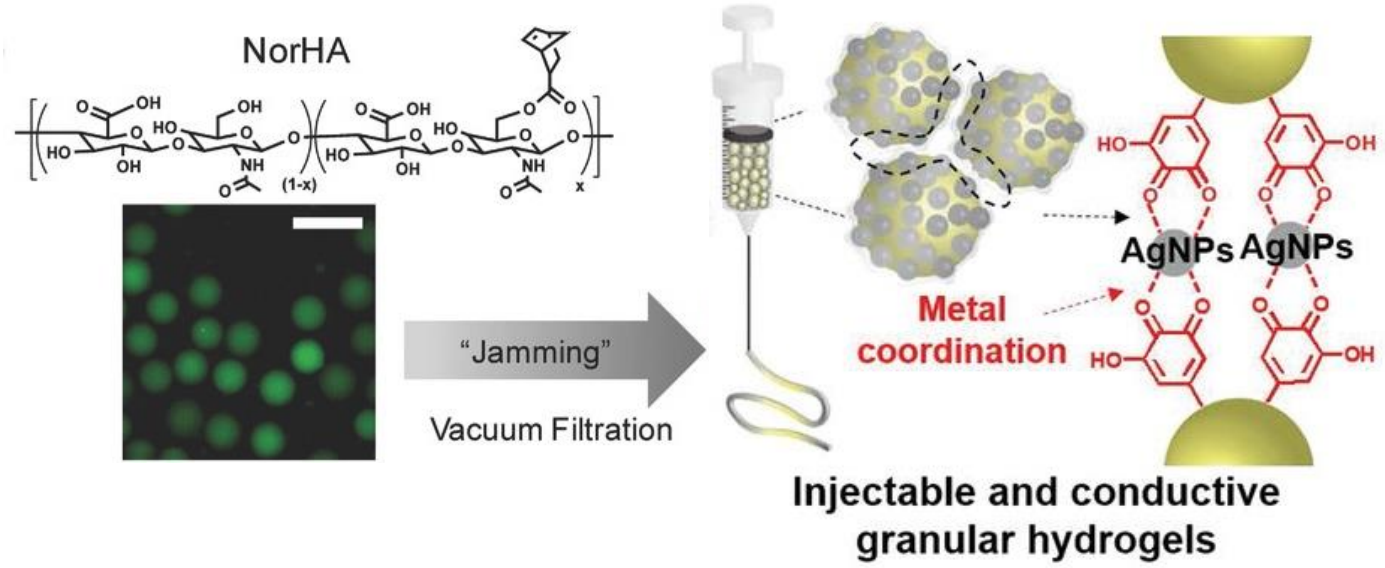
Self-healing



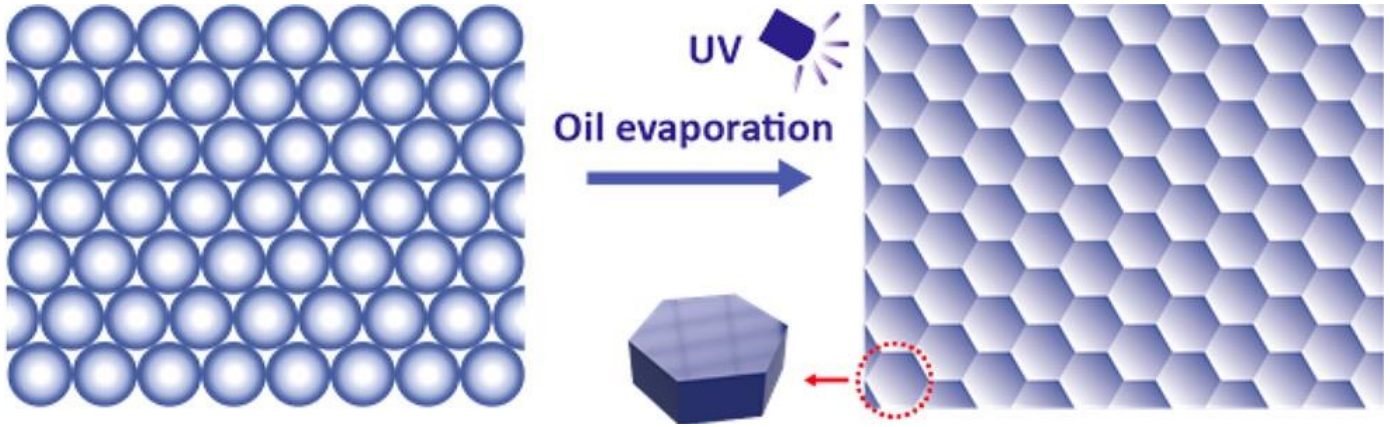
G' > G'' solid-like – G'' > G' liquid-like

Hirsch M., Charlet A., and Amstad E. *Advanced Functional Materials*, 2005929 (2020)

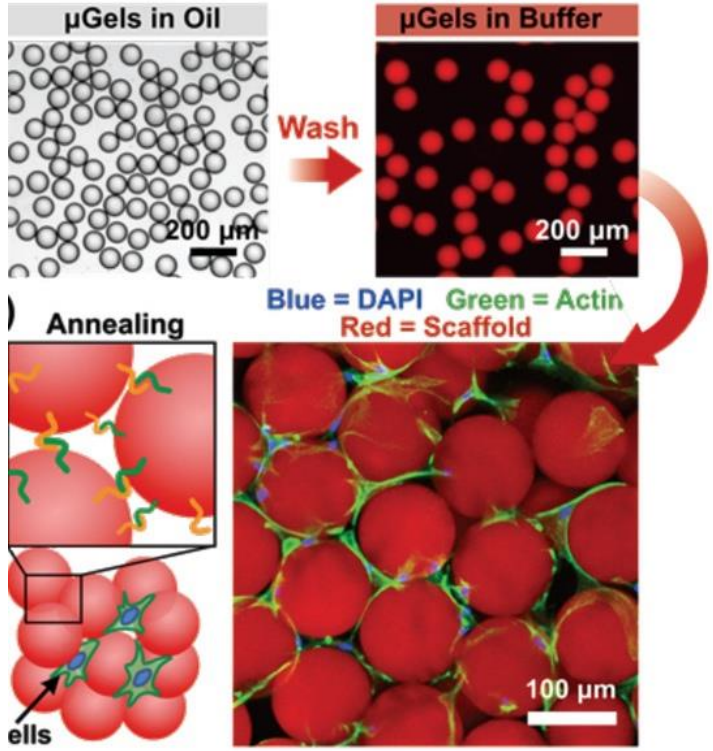
The Granular Hydrogel Dilemma



Adapted from: Shin, M. *et al.. Advanced Science*, 20, 1901229 (2019)



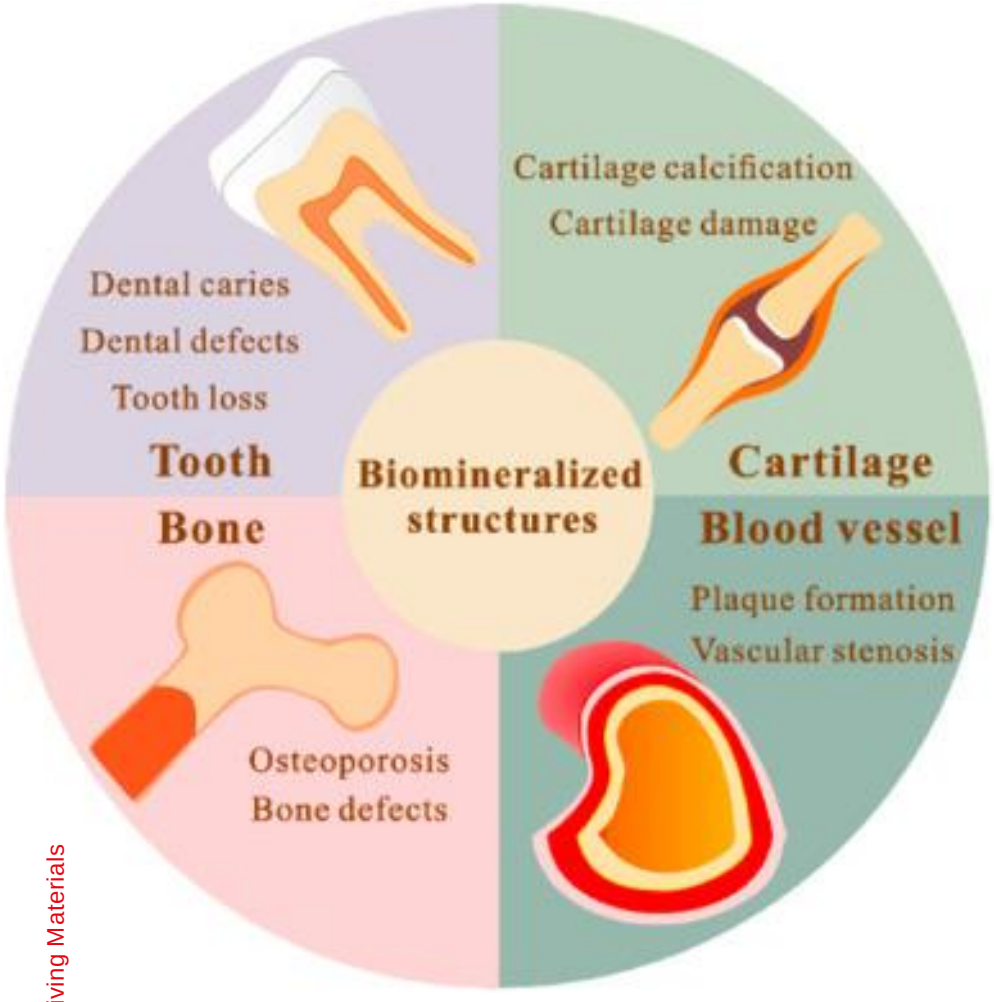
Du, H. *et al.. Langmuir*, 34, 7b04163 (2018)

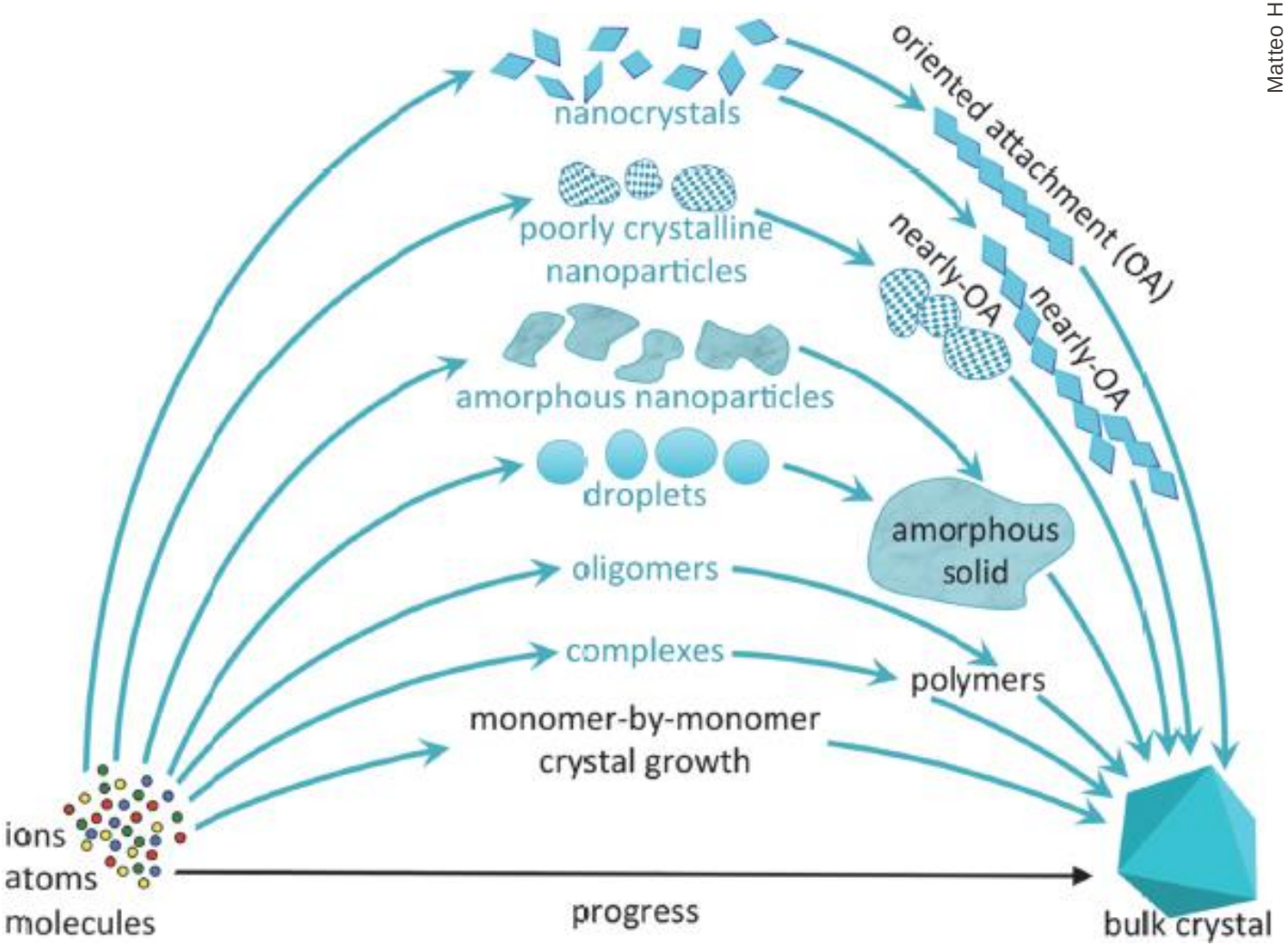


De Rutte, J. M. *et al.. Adv. Funct. Mat.*, 25, 1900071 (2019)

How can we get 3D printed granular structures with better mechanics?

Biomineralization





Biomineralization – is the process by which mineral crystals are deposited in the matrix of living organisms

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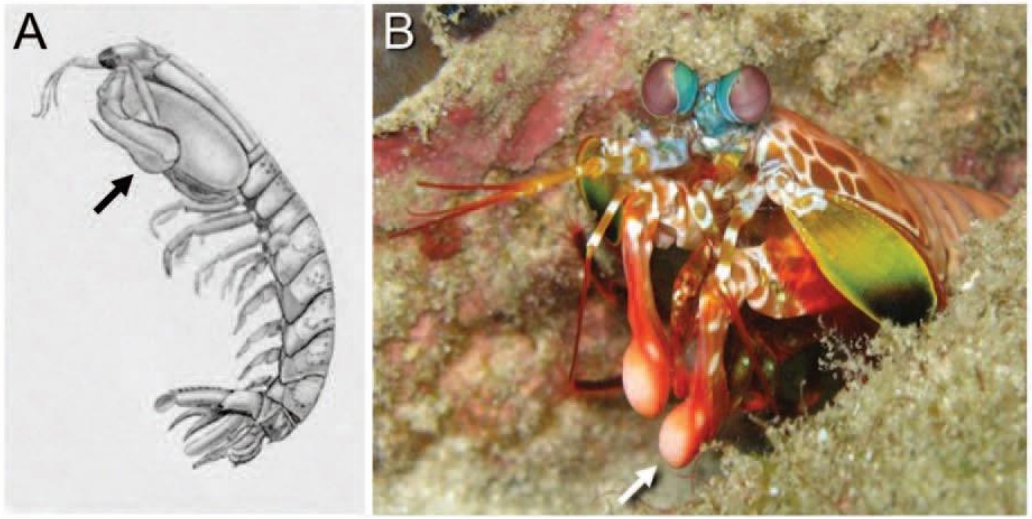
The Mantis Shrimp

https://youtube.com/clip/UgkxA-KYNpfQPluwuIei10RoFGXSQ3GLe1V1?si=-oF0EPUOQIH8Rs1x

The mechanical properties of the dactyl clubs

- Instantaneous forces ≥600 N
- high-velocity offensive strikes 80km/h
- strike completion time 1/50 s



A Formidable Damage-Tolerant Biological Hammer

The structural complexity of the dactyl clubs

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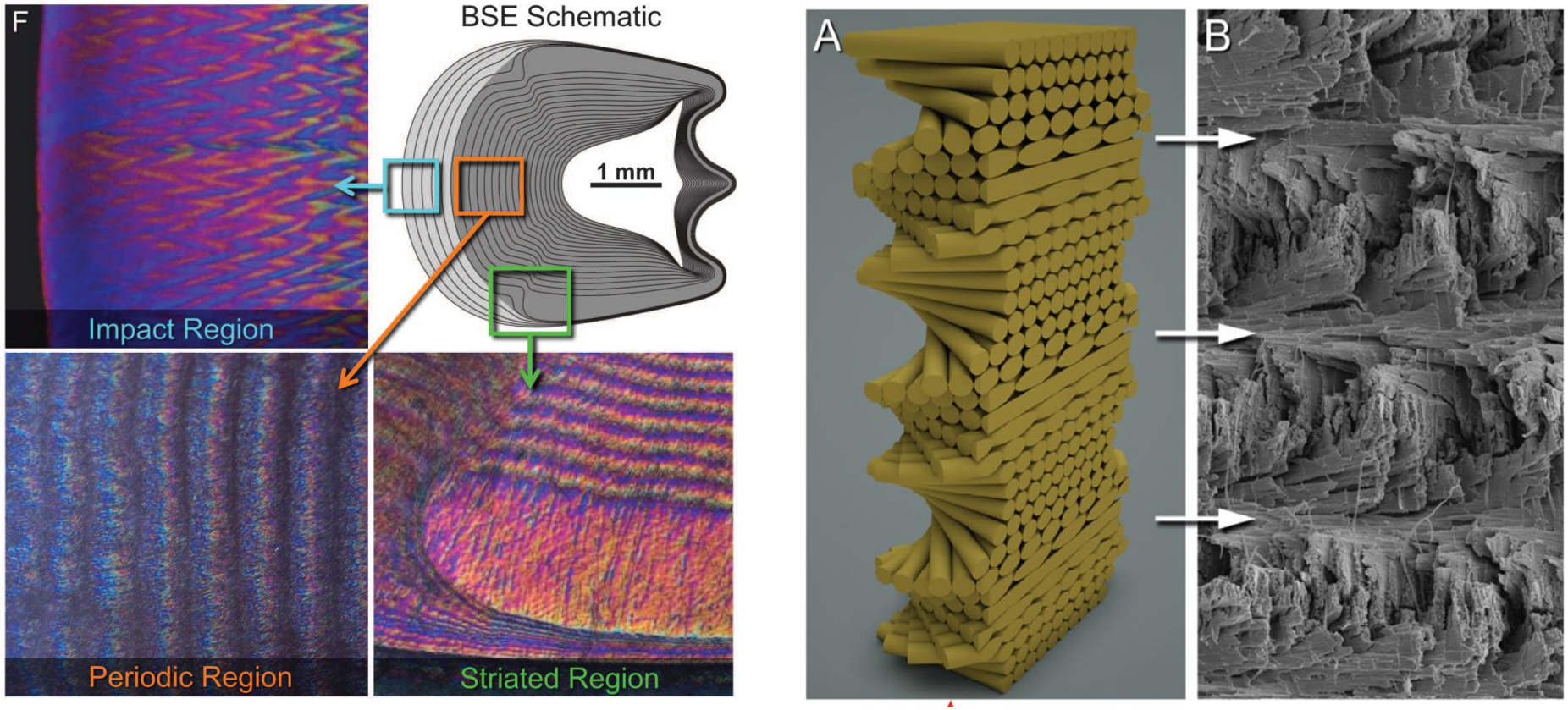
Three distinct structural domains:

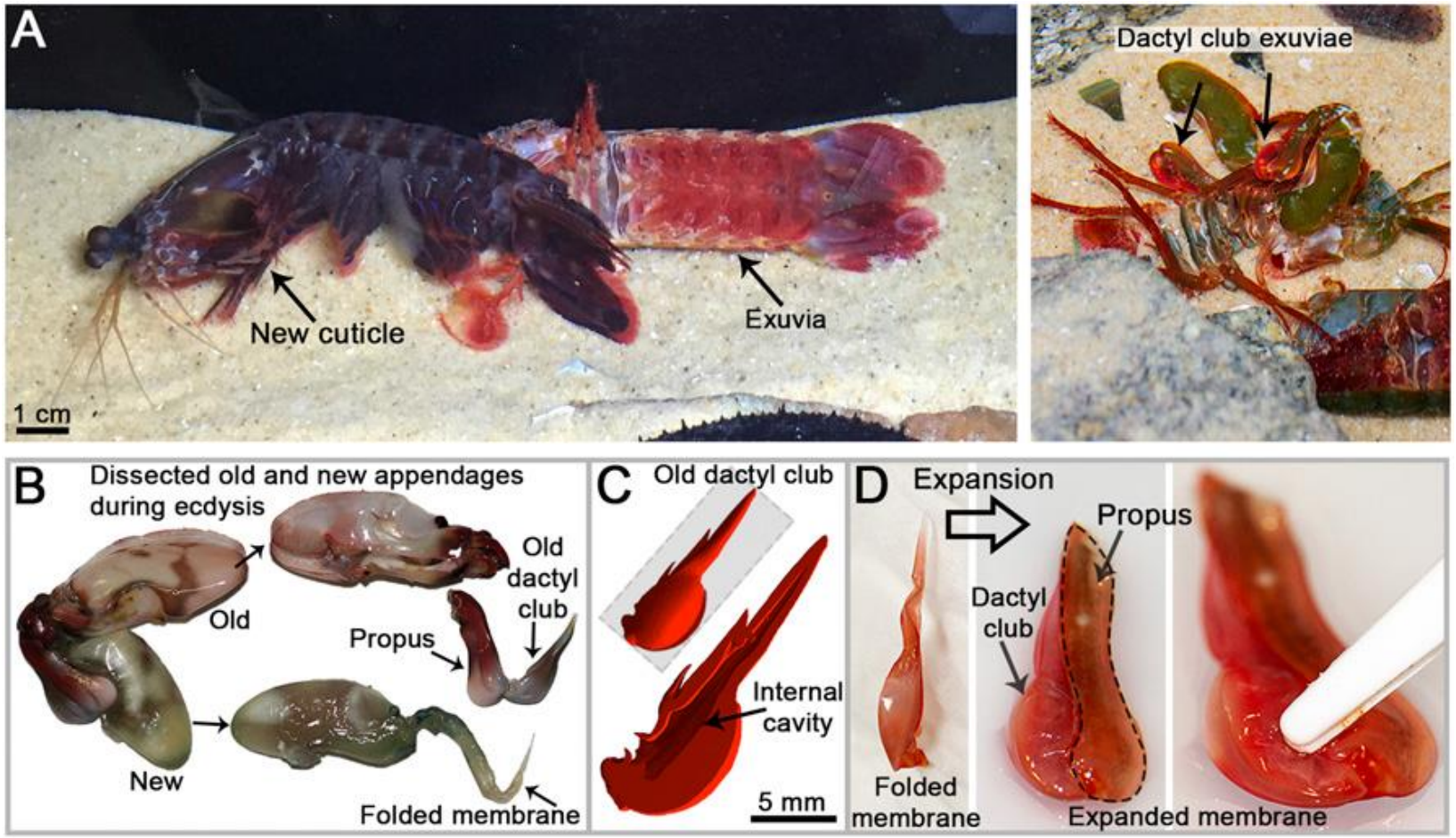
(i) The impact region (with orientated attached HAP/FAP nanoparticles),
(ii) The periodic region (with mineralized chitin fibril helicoidal structural motif),
(iii) The striated region (with the thickened circumferential band with parallel chitin fibers).



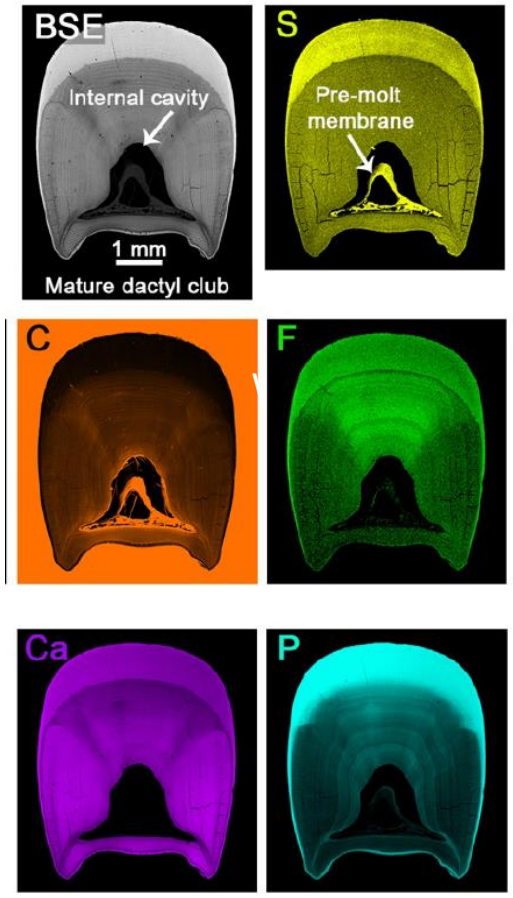
Science, 2012, 336(6086): 1275-1280.

Molting process

A flexible membrane initially folded within the club cavity expands to form the new club's envelope.



In the premolt membrane



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Diecast mineralization process

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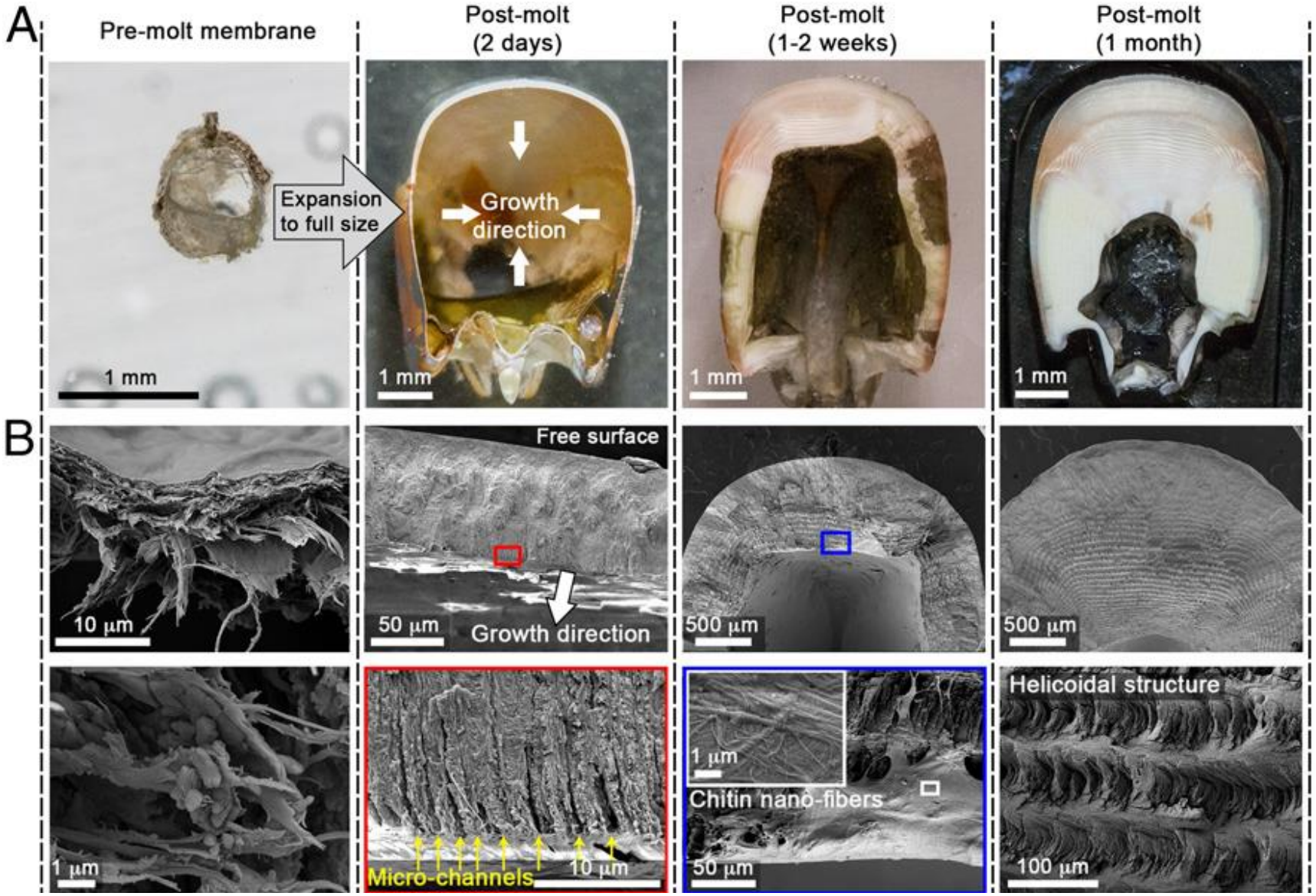
Structure of the dactyl club at various time points of the molting and formation process



Diecast mineralization process

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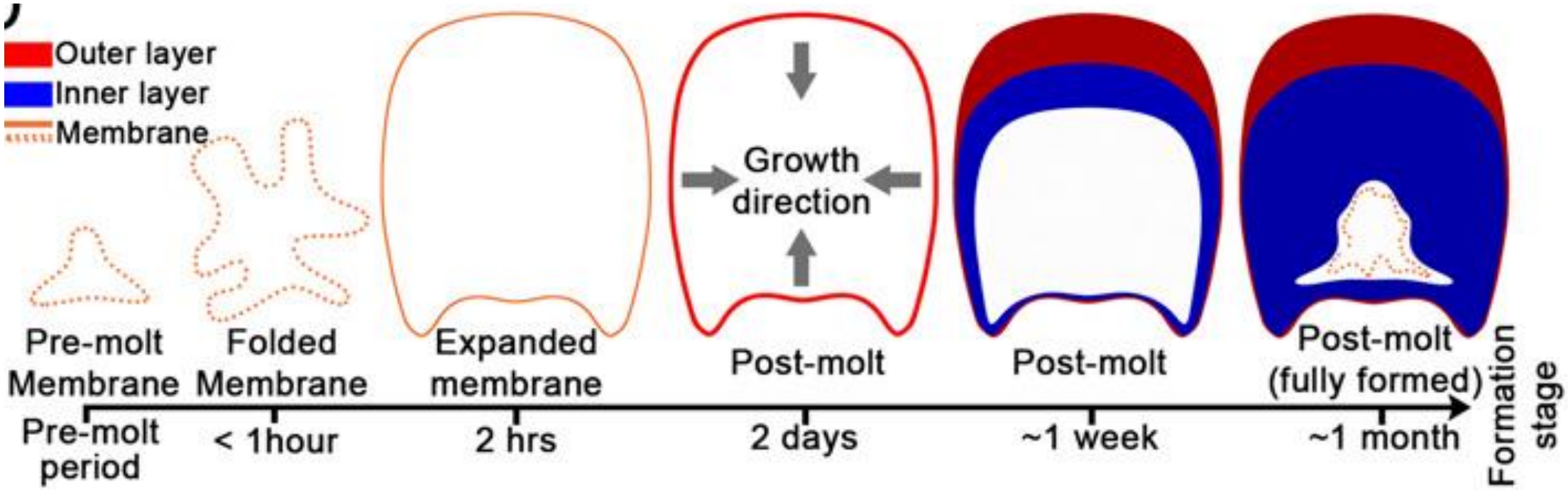
Schematic of the formation process of the dactyl club during the first month after ecdysis



Structural Formation and Mechanical Stiffening

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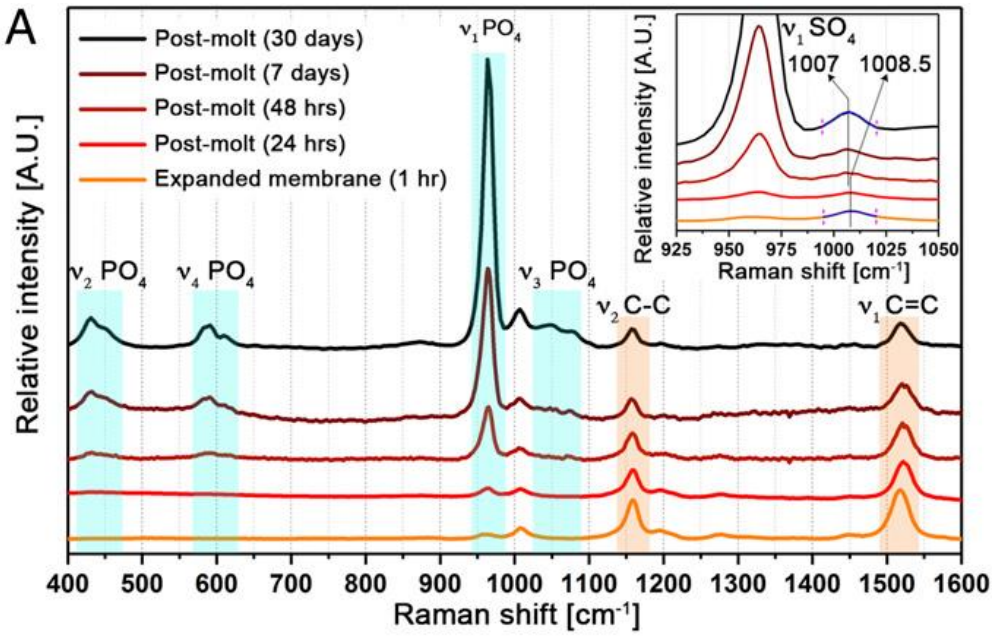
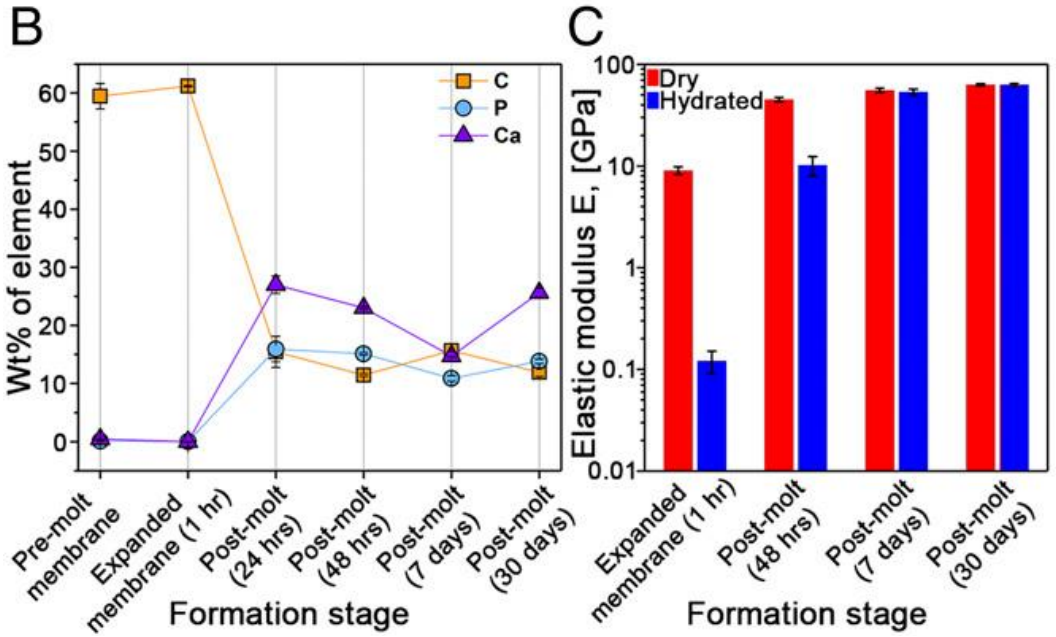
Raman spectroscopy, EDS analysis, and nanomechanical measurements





Fluorapatite (v1 vibration mode at 965 cm−1)
Proteins and chitin ~1,160 cm−1 and 1,520 cm−1
Calcium sulfate (v1 peak at 1,007 cm−1)

E_{1hr} = 0.12 ± 0.03 GPa
E_{48hr} = 10.2 ± 2.2 GPa
E_{1week} = 53.5 ± 3.6 GPa
E_{mature} = 62.8 ± 1.9 GPa

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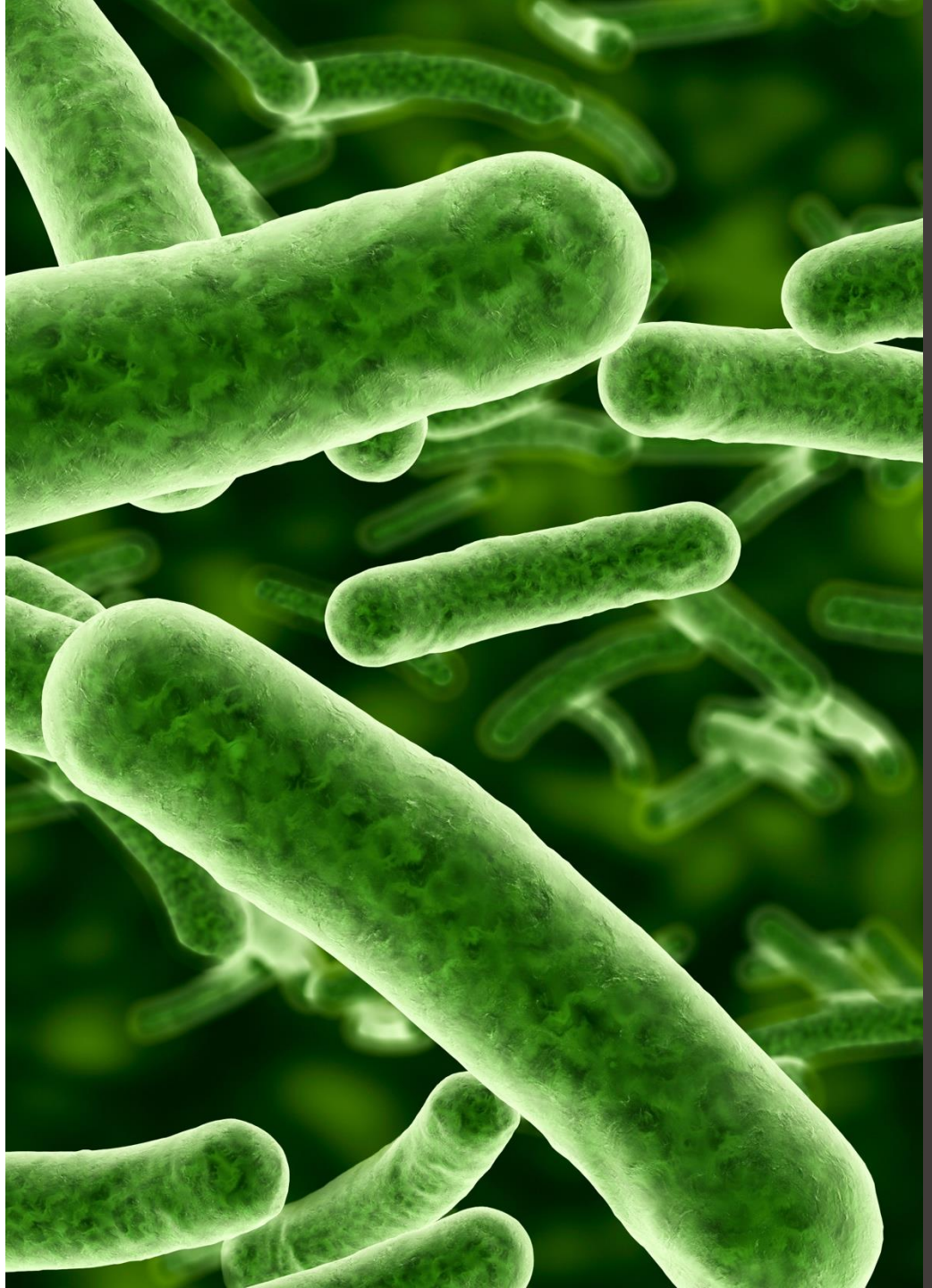
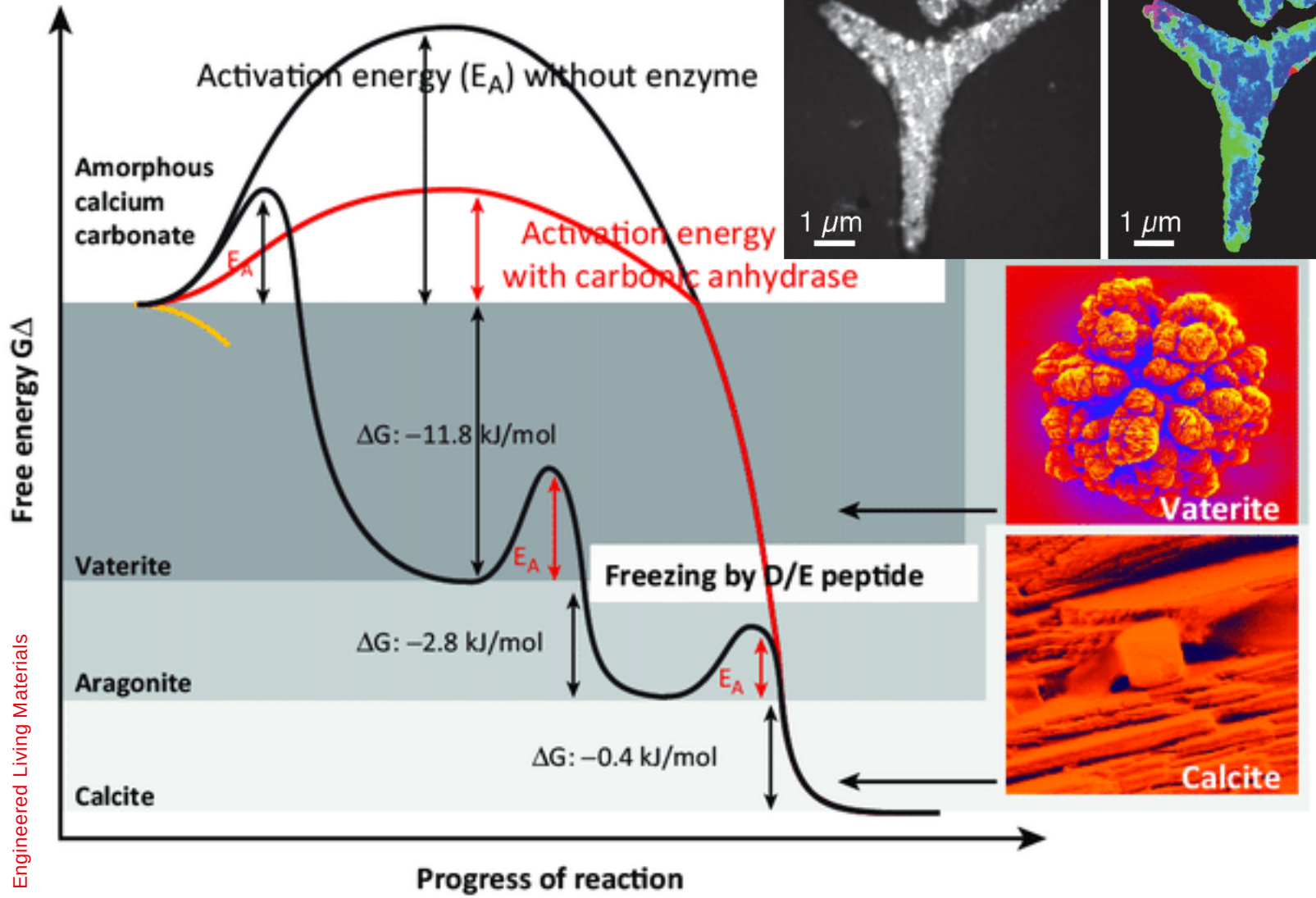
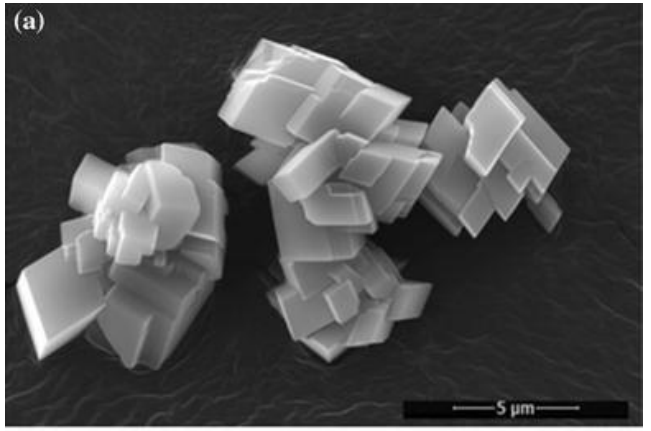


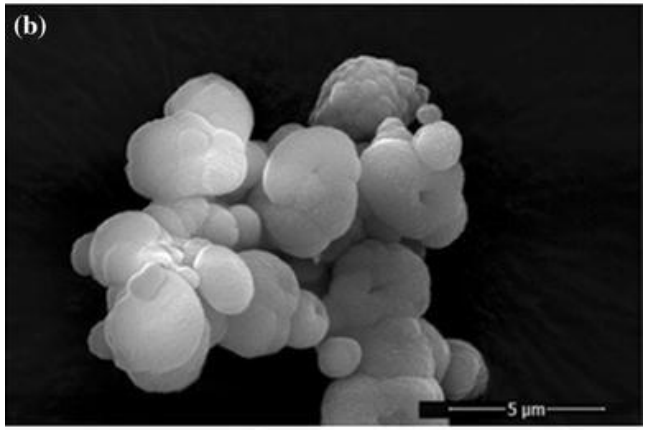
3D Printing of Living Structural Biocomposites

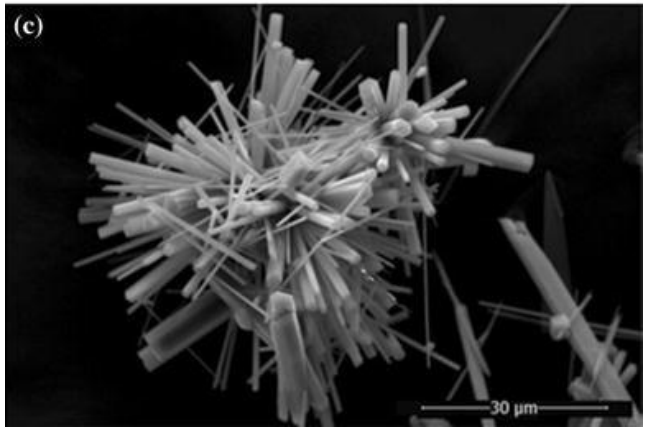
https://www.news.uzh.ch/en/articles/2019/forensik-bakterien.html

Calcium Carbonate Polymorphs









Adapted from: Du, H. *et al. CHIMIA*, 173, 1/2 (2019)

Natural Materials and Bioinspiration

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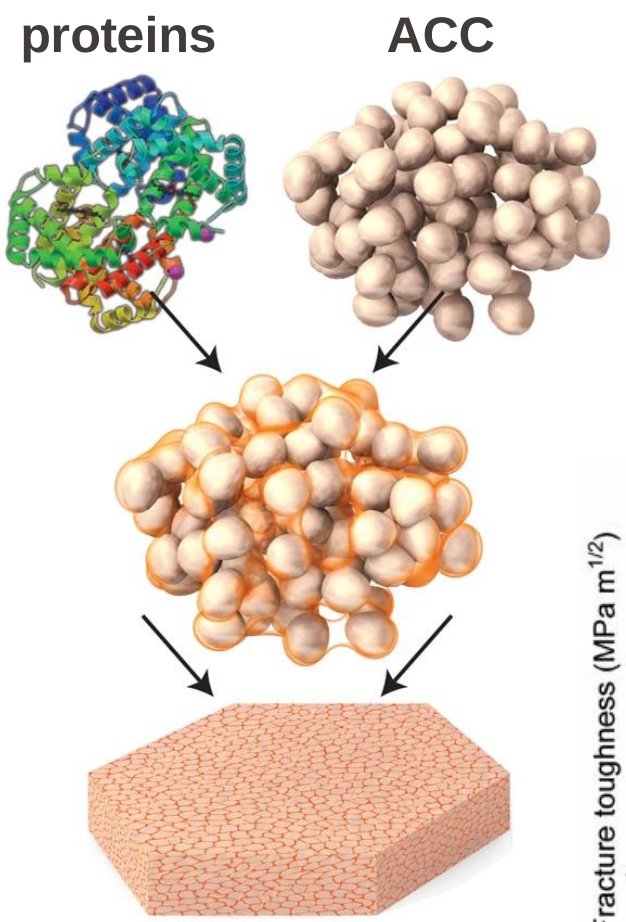
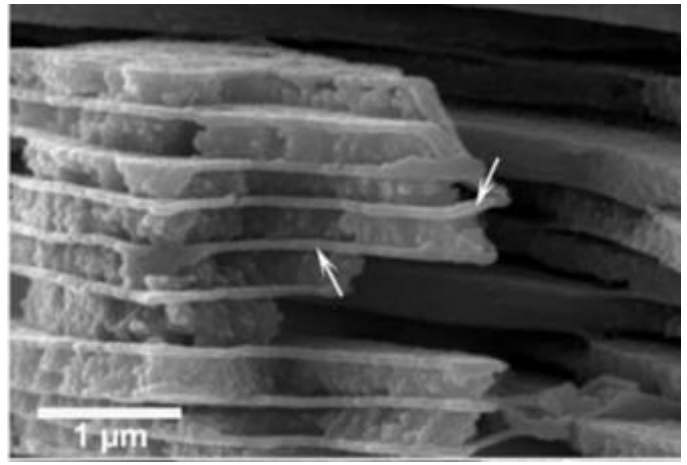
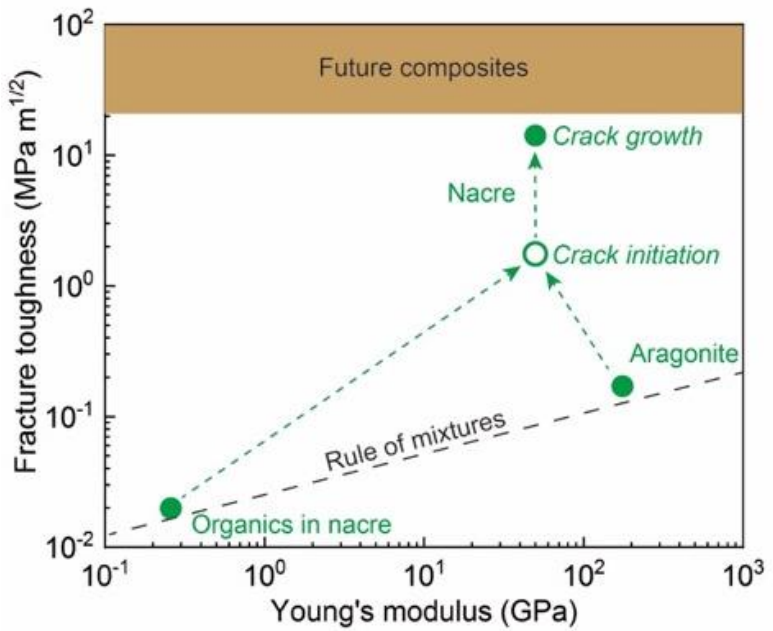




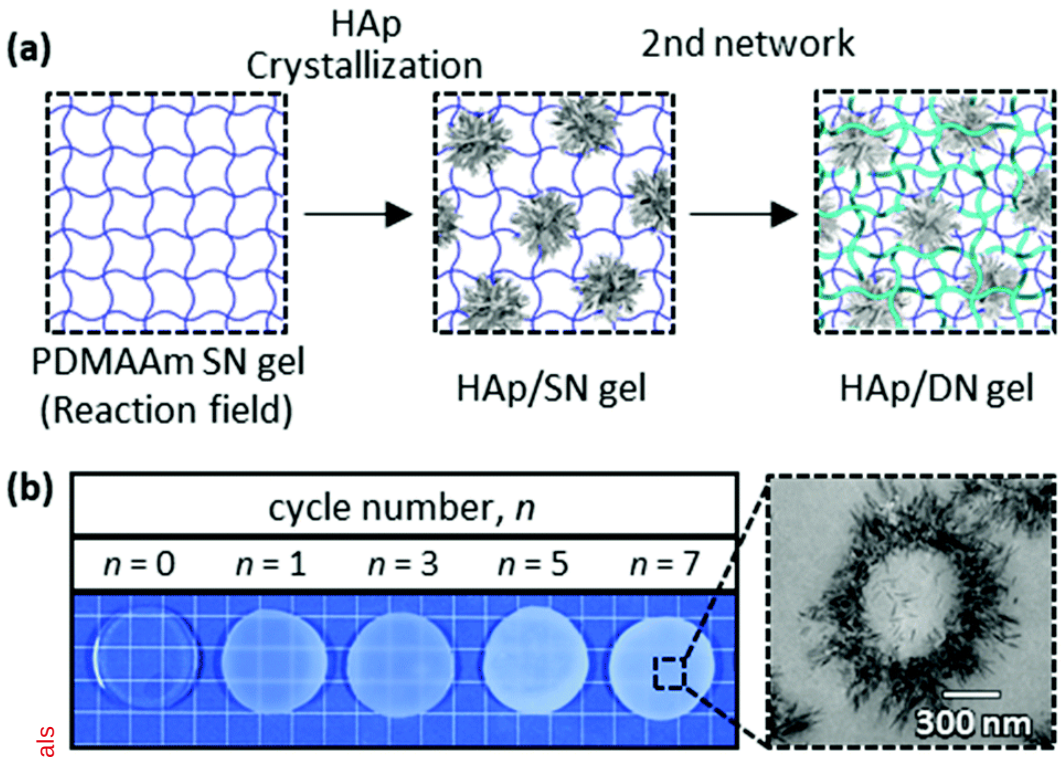
The fascinating mechanical properties of nacre are a result of the unique combination of well-defined hierarchical structure and local varying composition

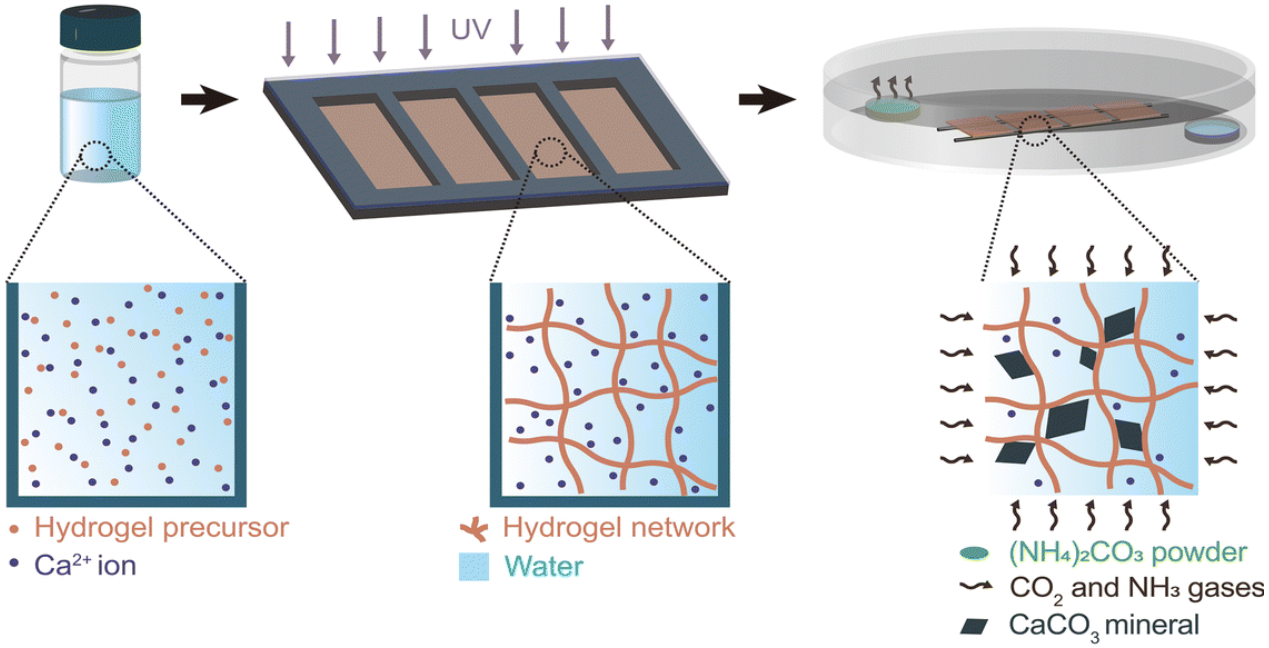


Adapted from: Wegst, U. G. K. *et al. Nature Materials*, 14, 1 (2015) – Du, H. *et al. CHIMIA*, 173, 1/2 (2019)

Bioinspired Approach

Matteo Hirsch





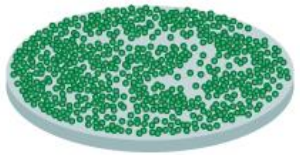
Final biomineral content is limited by the diffusion of reactants through the hydrogel network

Adapted from: Fukao K., *et al. Journal of Materials Chemistry B*, 8, 24 (2020) – Du, H. *et al. Biomaterials Science* (2022)

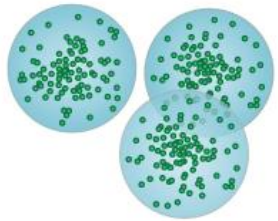
Engineered Living Materials

Matteo Hirsch

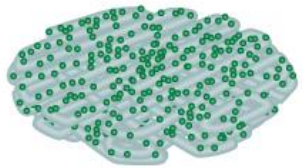
Processing



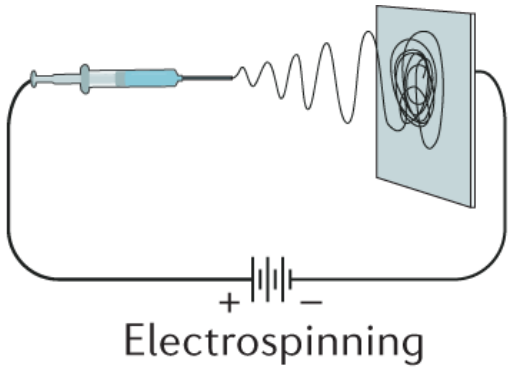
Surface adhesion (biofilms)



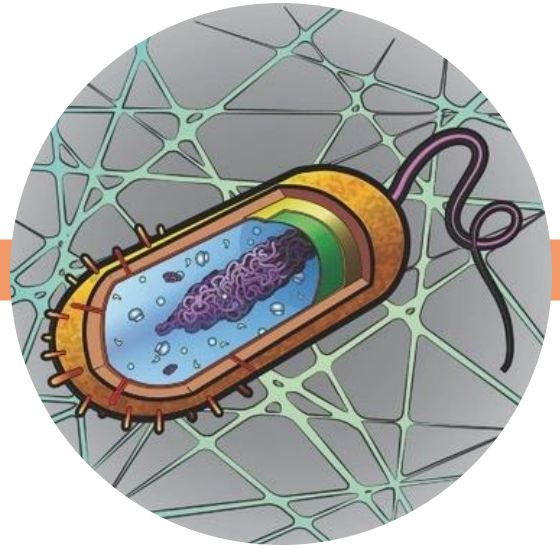
Microgels



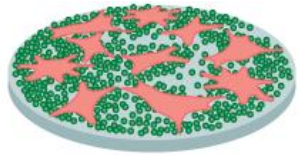
3D printing



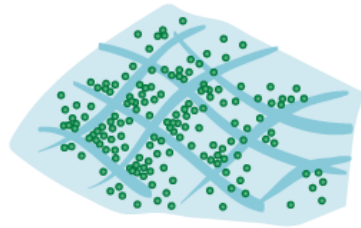
Electrospinning



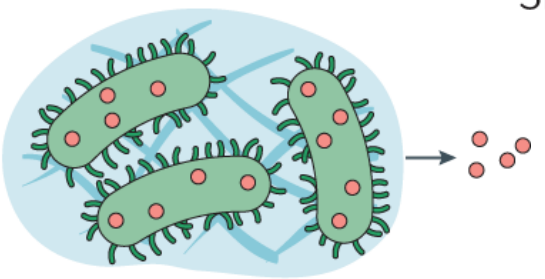
Applications



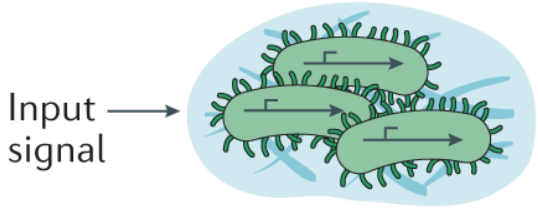
Living biointerfaces



Skin patches



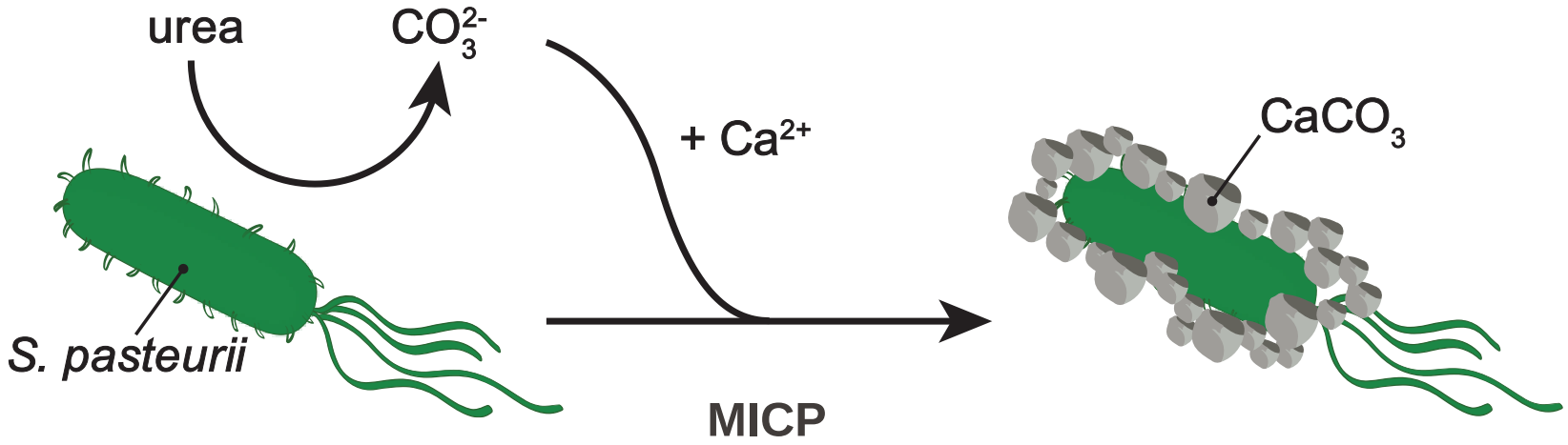
Drug release

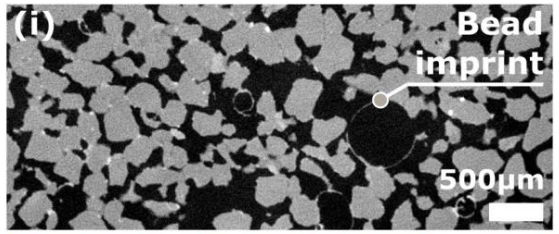


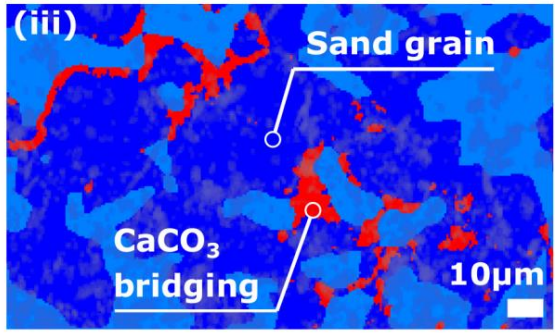
Biosensors

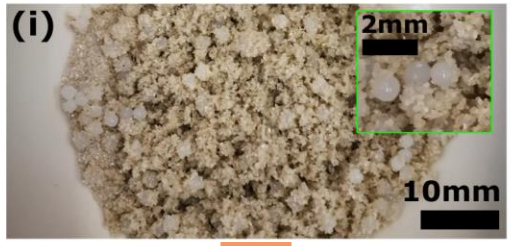
Adapted from: Rodrigo-Navarro, A. *et al. Nature Review Materials*, 6, 1175 (2021)

Microbiologically Induced Calcite Precipitation









urease

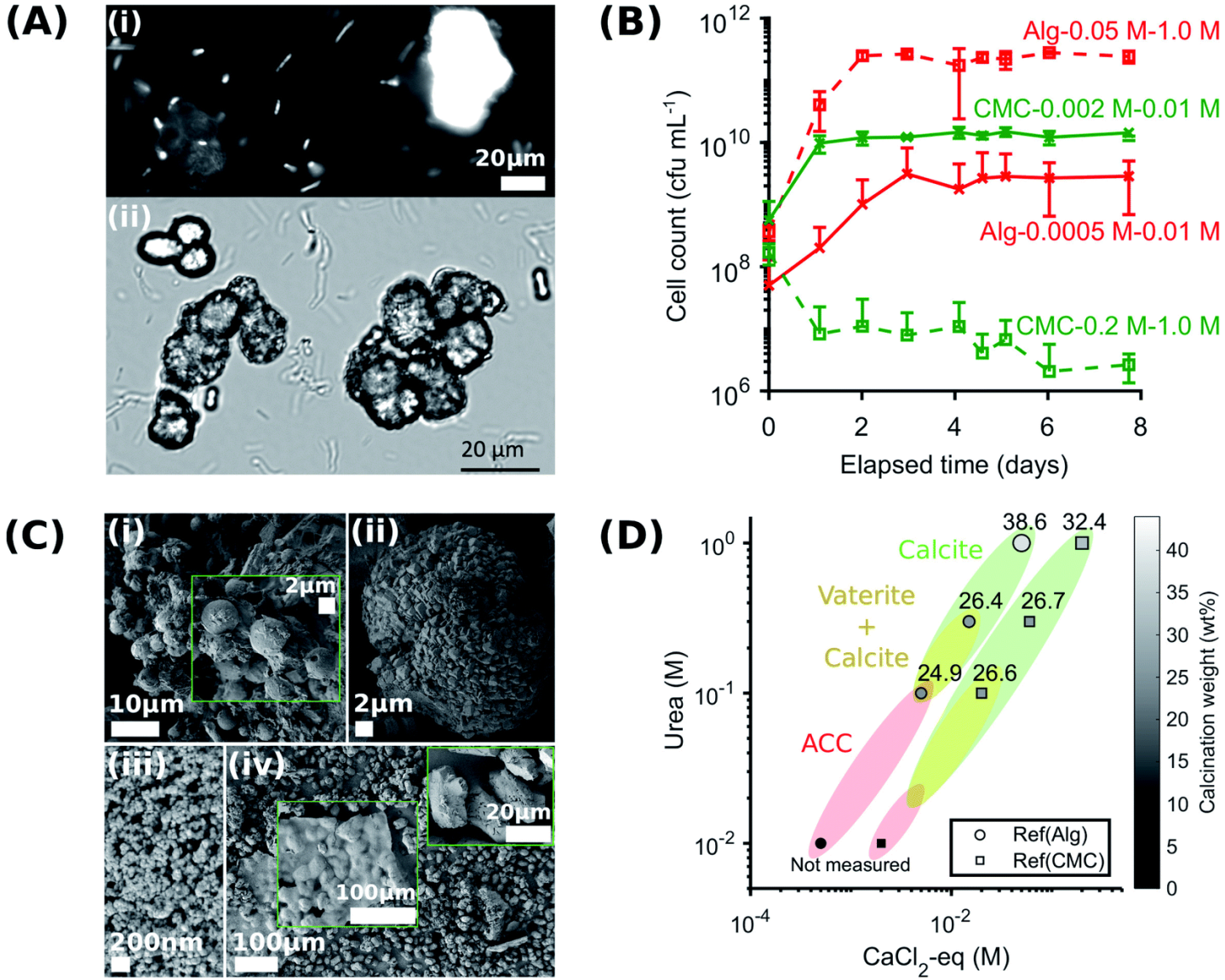
$$1)\ CH_4N_2O + 2H_2O \xrightarrow{\text{urease}} 2NH_4^+ + CO_3^{2-}$$

$$2)\ Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow$$

- Class I bacteria, gram positive
- High urease activity
- Widely adopted in Geotech

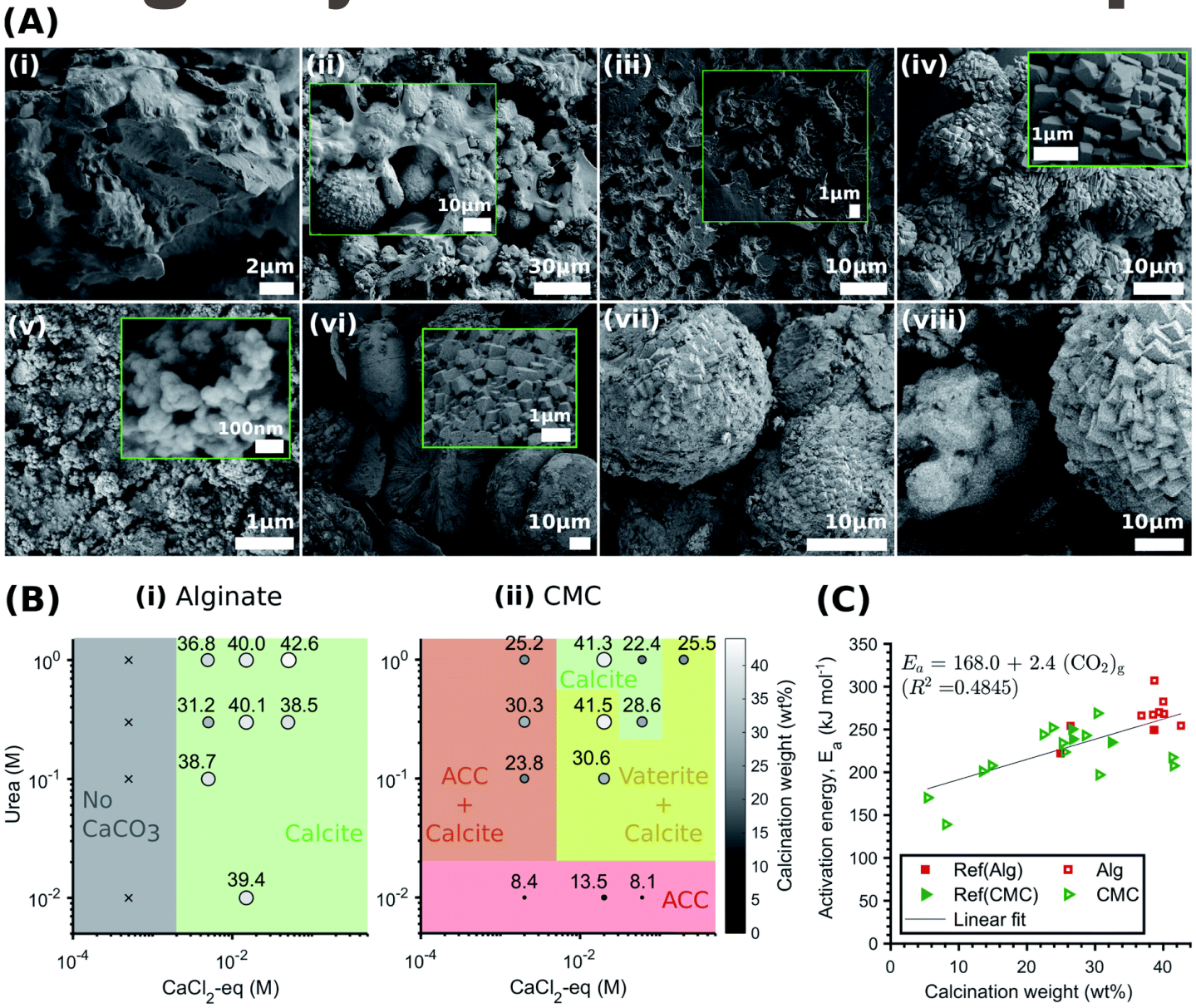
Clarà Saracho A., Lucherini L., **Hirsch M.**, Peter H., Terzis D., Amstad E., and Laloui L. *Journal of Materials Chemistry A.* (2021)

Microbiologically Induced Calcite Precipitation



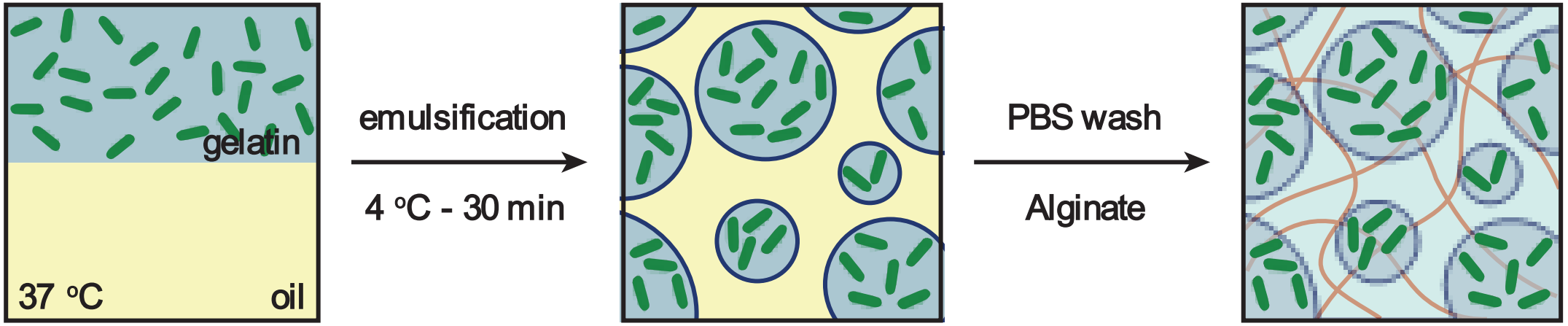
Clarà Saracho A., Lucherini L., **Hirsch M.**, Peter H., Terzis D., Amstad E., and Laloui L. *Journal of Materials Chemistry A.* (2021)

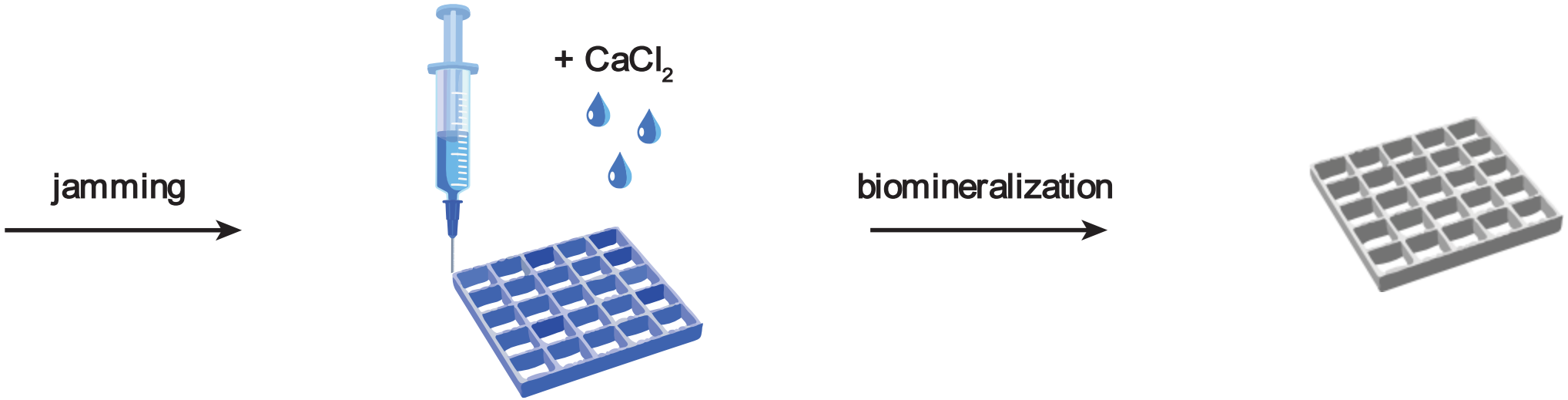
Microbiologically Induced Calcite Precipitation



Clarà Saracho A., Lucherini L., **Hirsch M.**, Peter H., Terzis D., Amstad E., and Laloui L. *Journal of Materials Chemistry A.* (2021)

Bacteria-Loaded Microgel Printing



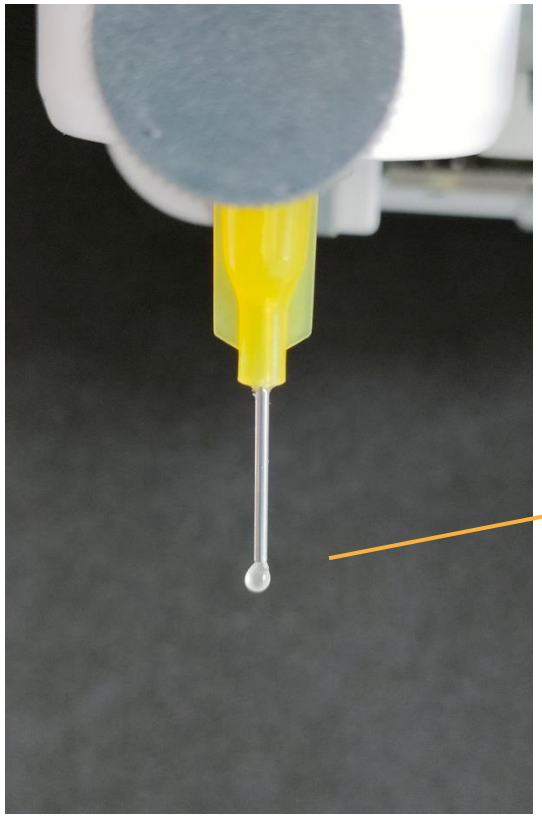


Hirsch M., Lucherini L., Zhao R., Clarà Saracho A., and Amstad E. *Materials Today (2023)*

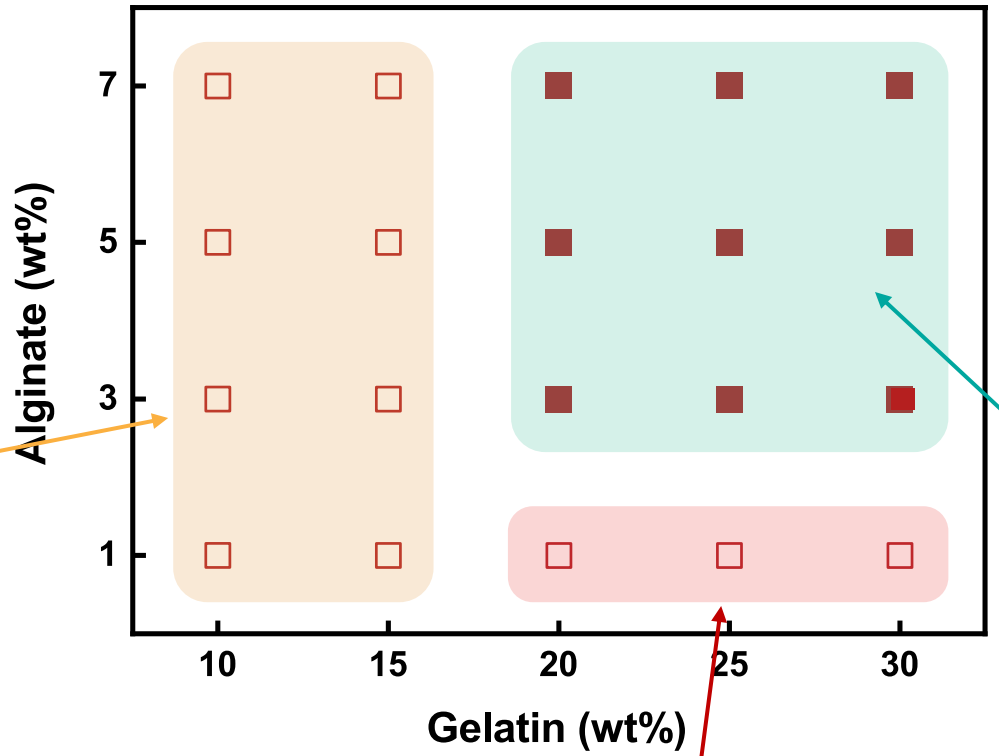
Matteo Hirsch

3D Printing of Bacteria-Loaded Jammed Microgels

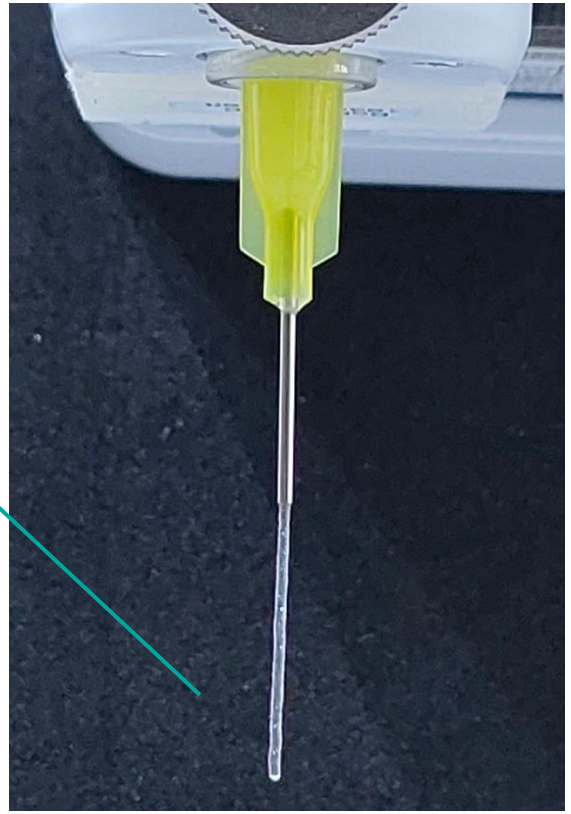
Matteo Hirsch



Dripping



Not stable



Extrusion

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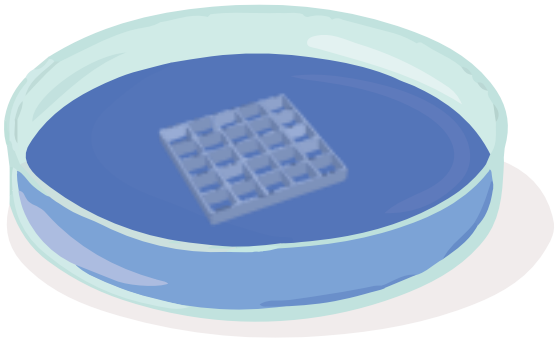
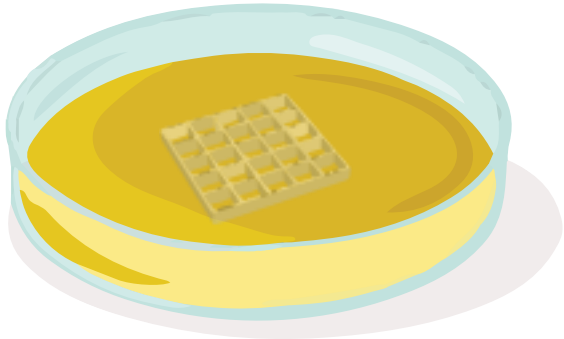
Biomineralization of 3D Printed Scaffolds

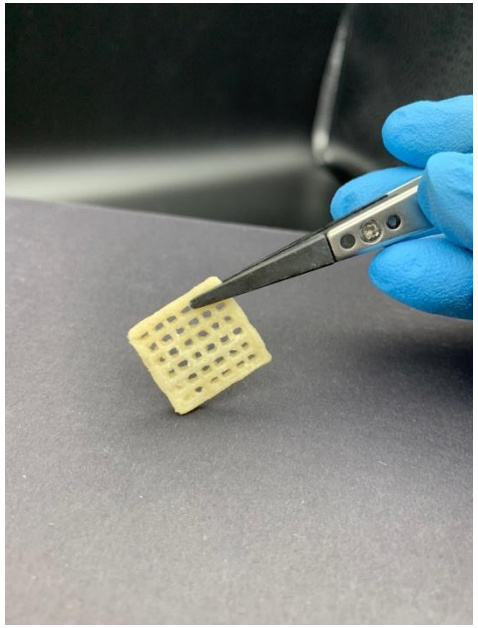


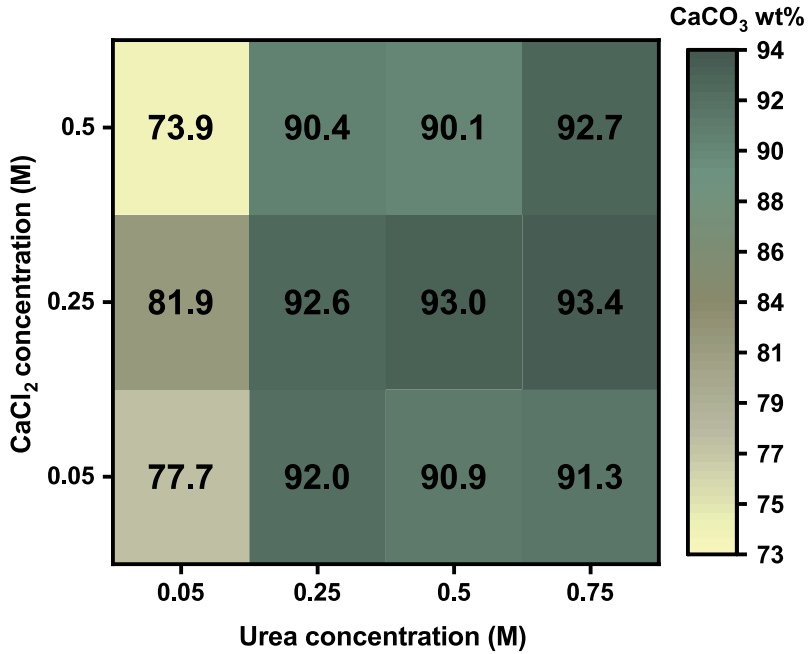
biomineralization



$CaCl_2$ solution

YUT media





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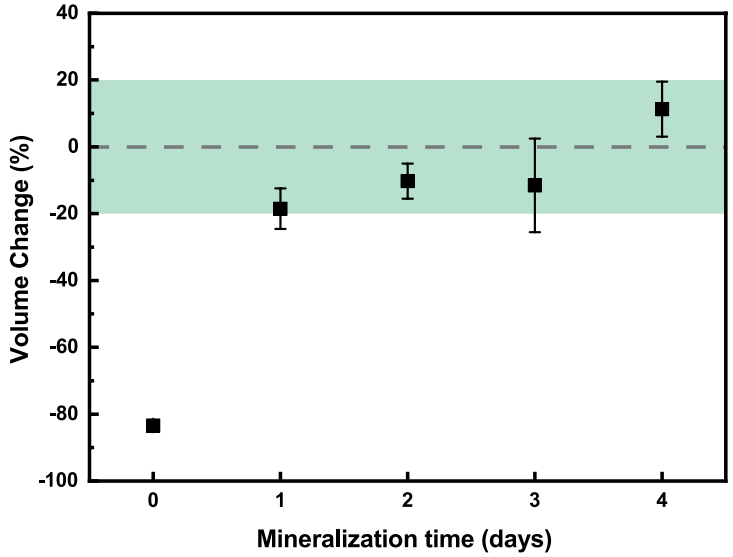
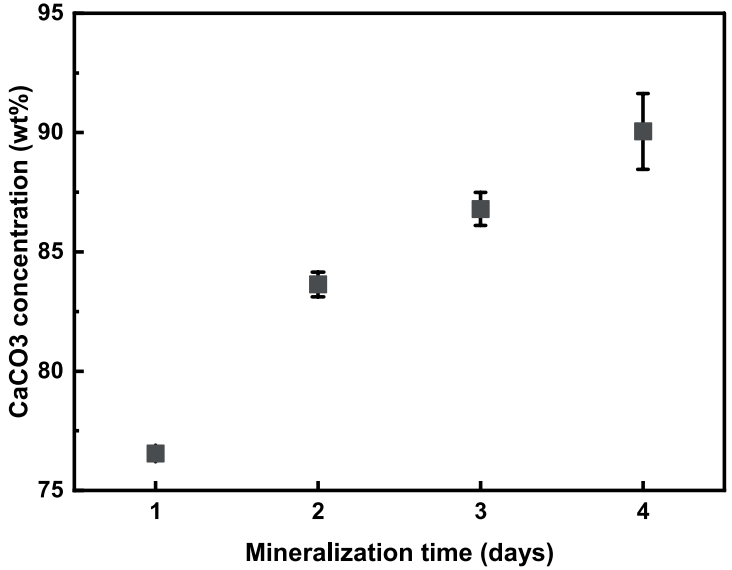
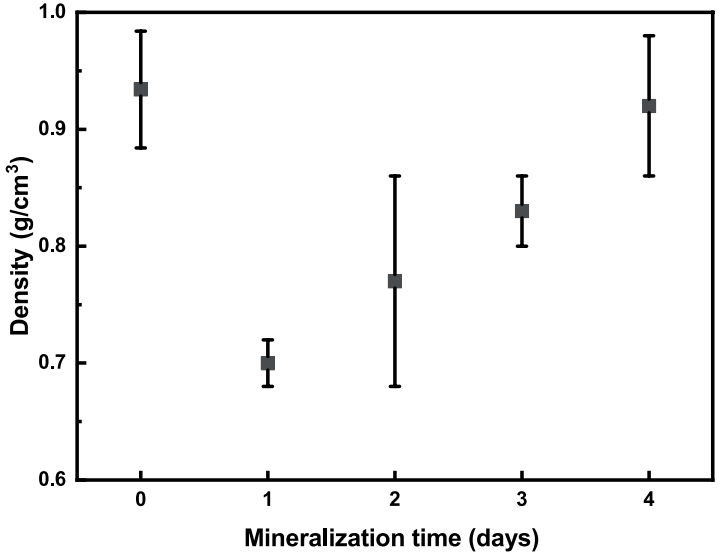
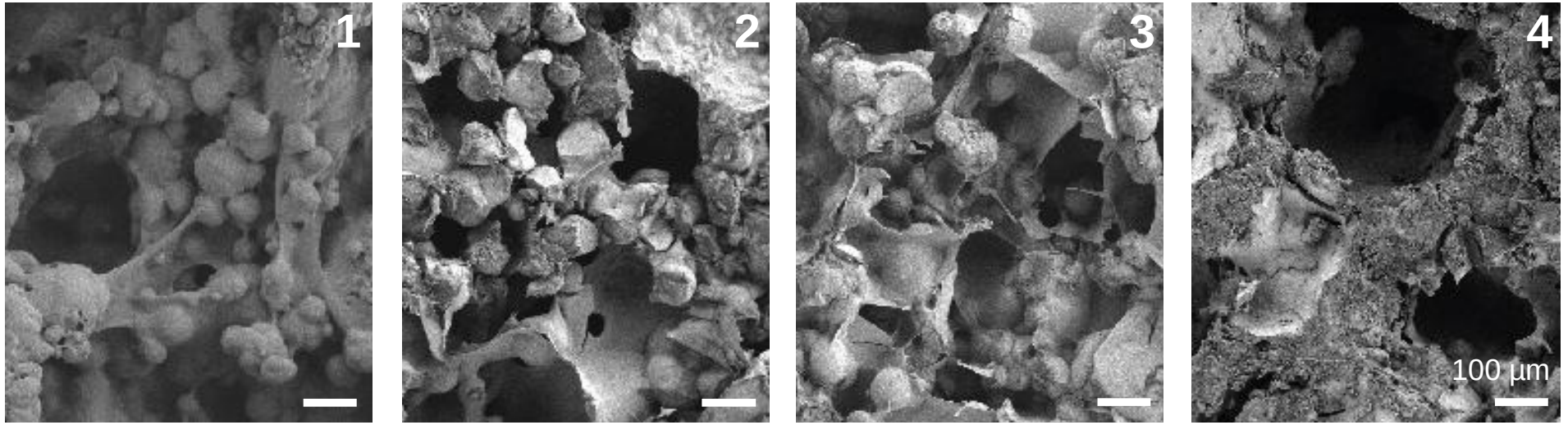
Biomineralization of 3D Printed Scaffolds

Matteo Hirsch









Volume change is inhibited due to biomineral precipitation

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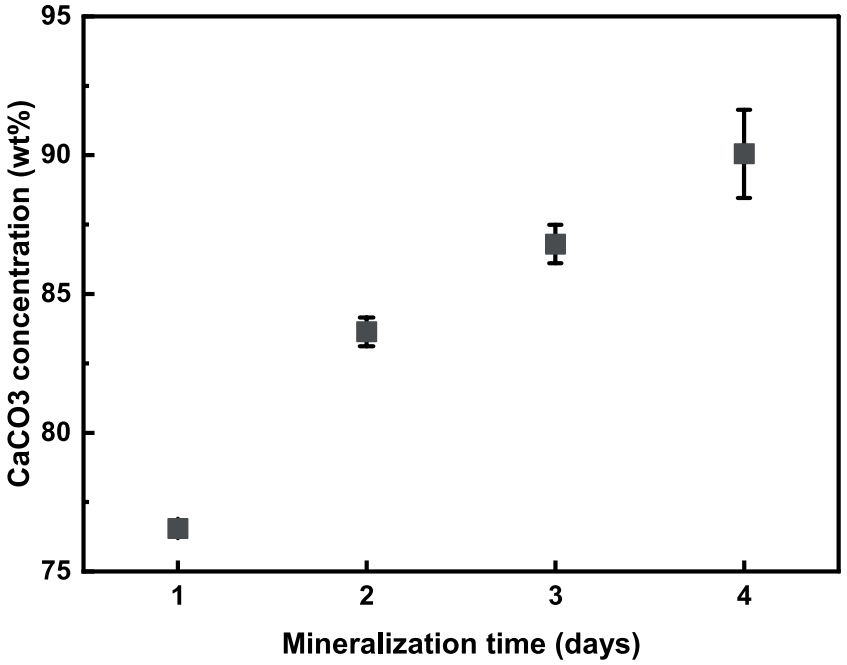
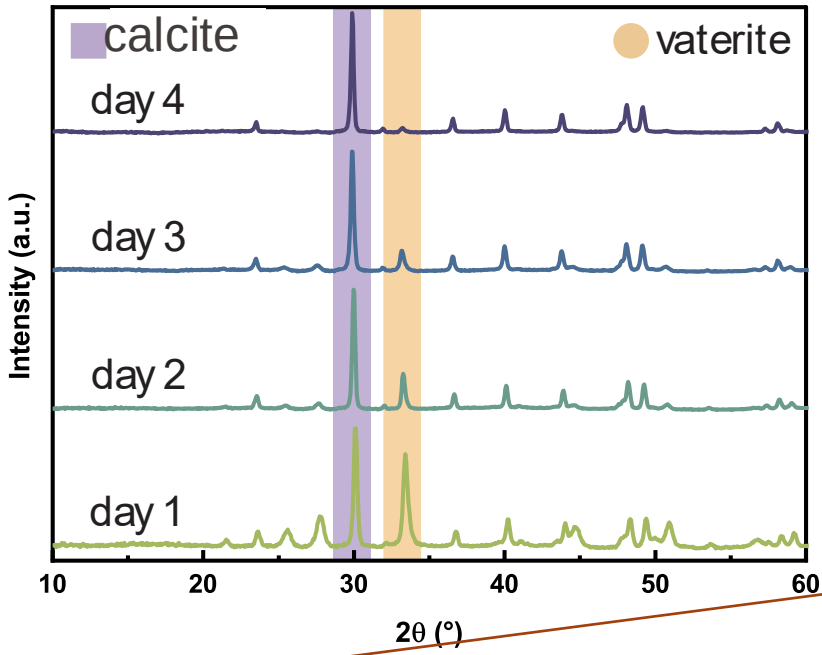
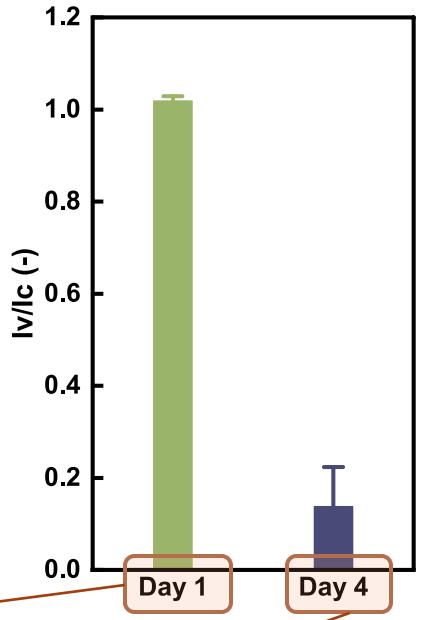
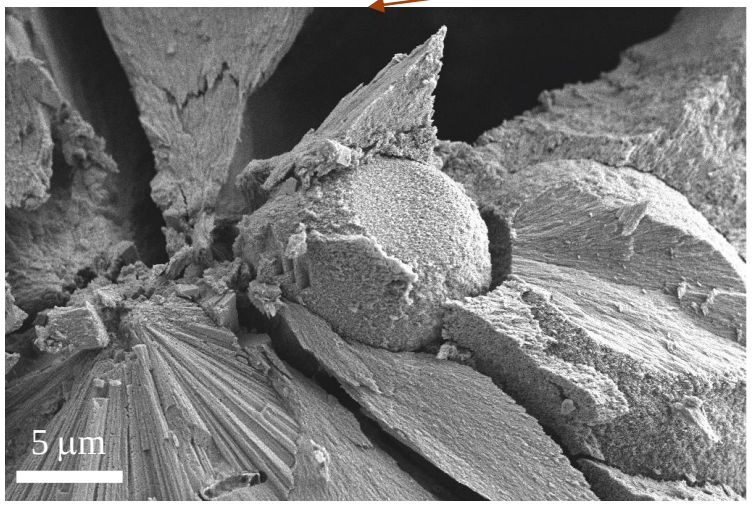
Biomineralization of 3D Printed Scaffolds

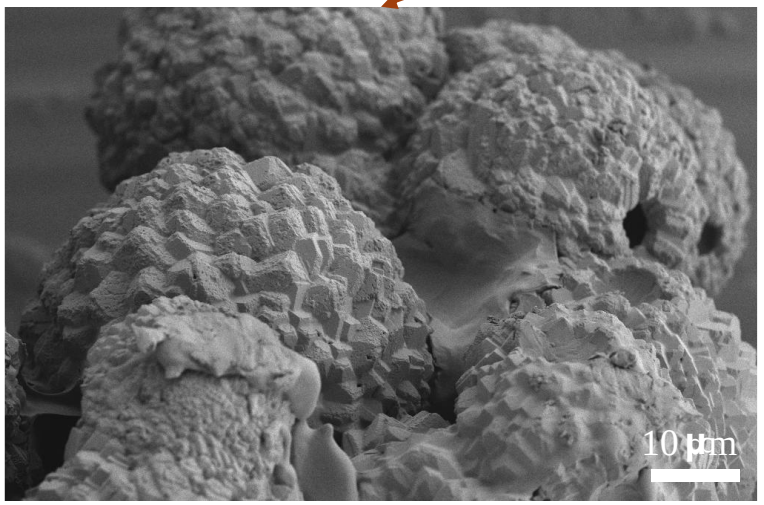
Matteo Hirsch







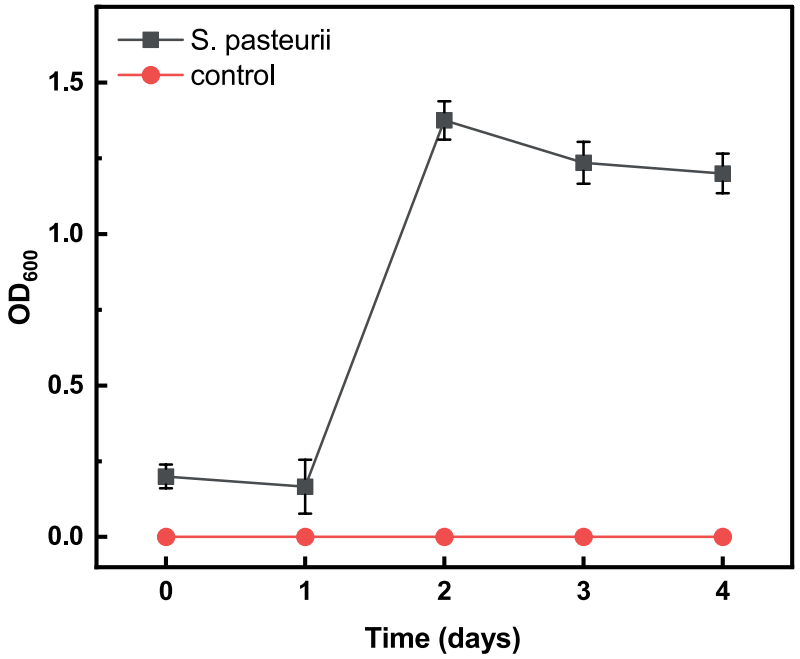


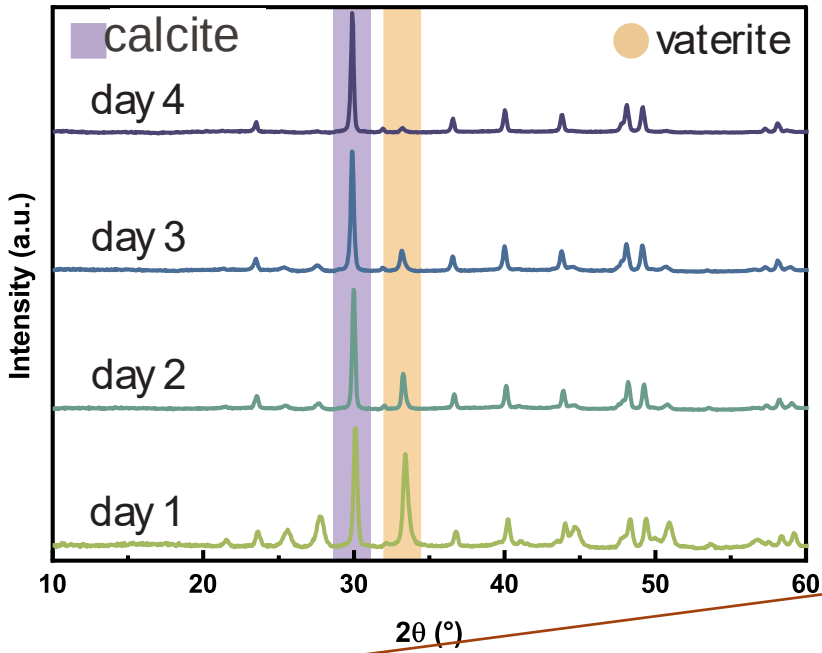


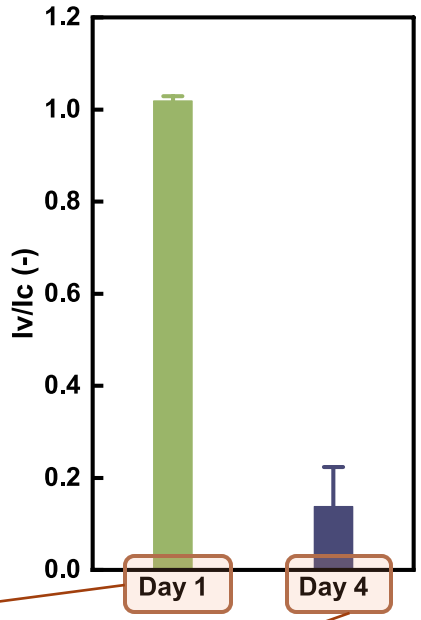
Hirsch M., Lucherini L., Zhao R., Clarà Saracho A., and Amstad E. *Manuscript submitted*

Biomineralization of 3D Printed Scaffolds

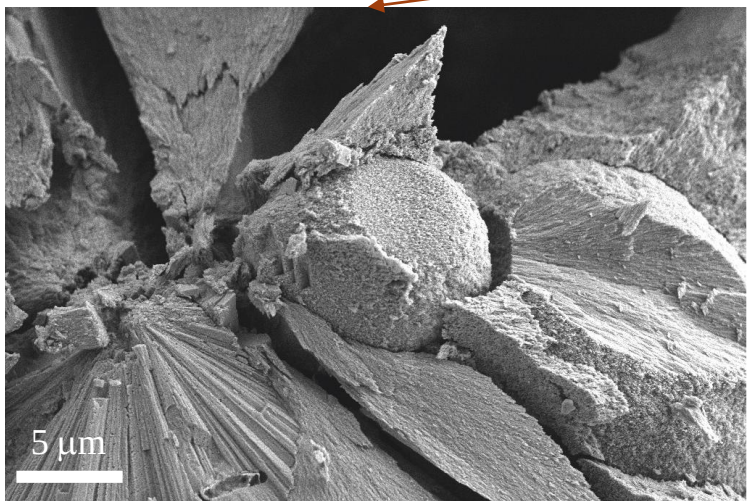
Matteo Hirsch

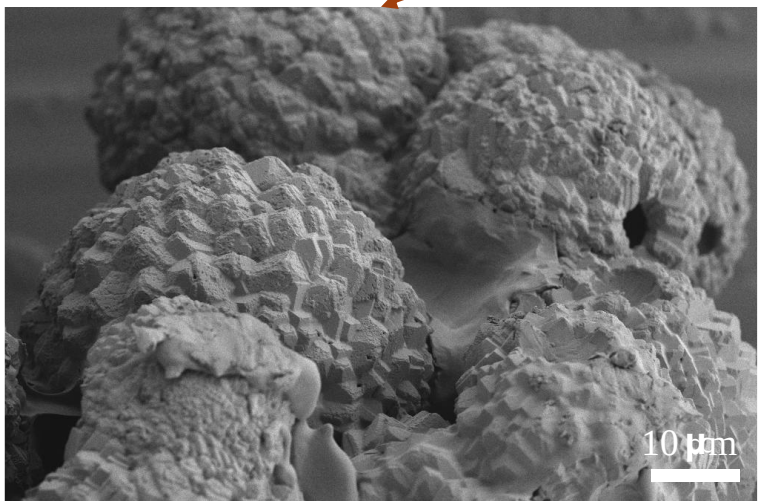






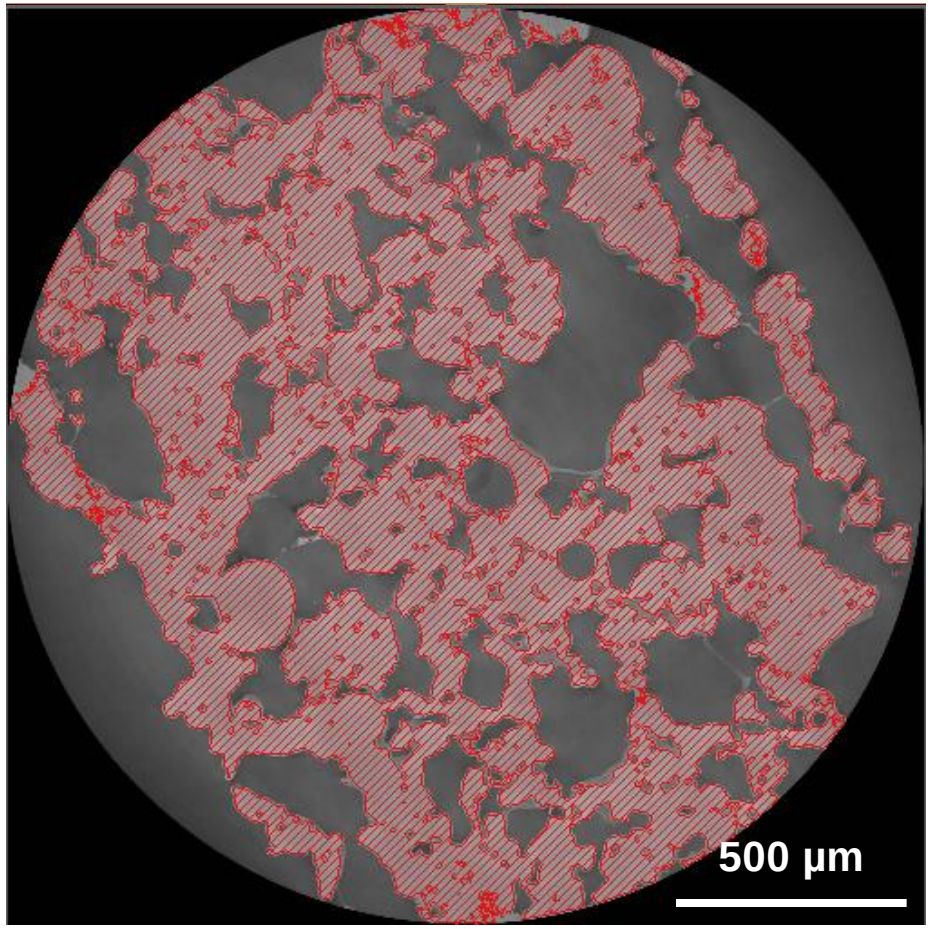
Initial precipitation of vaterite due to low bacteria activity in the first 24h

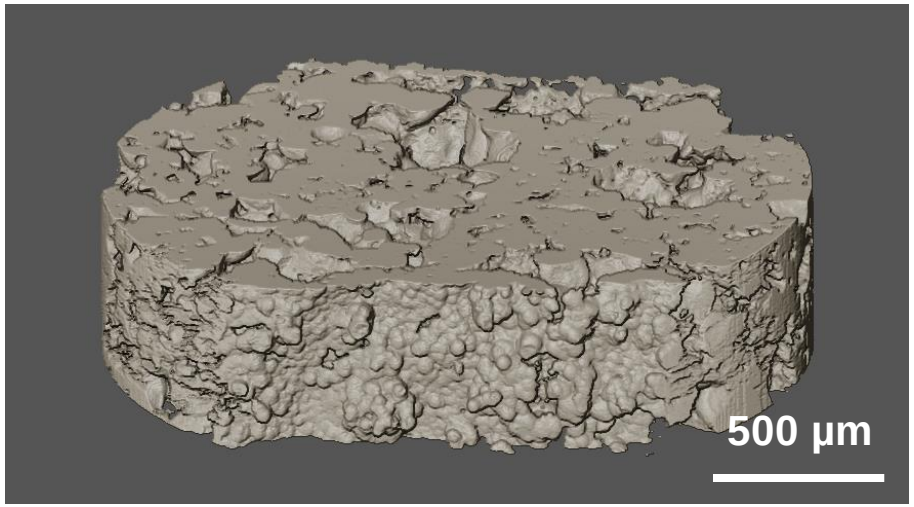




Hirsch M., Lucherini L., Zhao R., Clarà Saracho A., and Amstad E. *Manuscript submitted*

Micro Tomography of Biomineralized Scaffold





µCT confirms the presence of mineral bridges and microporosity

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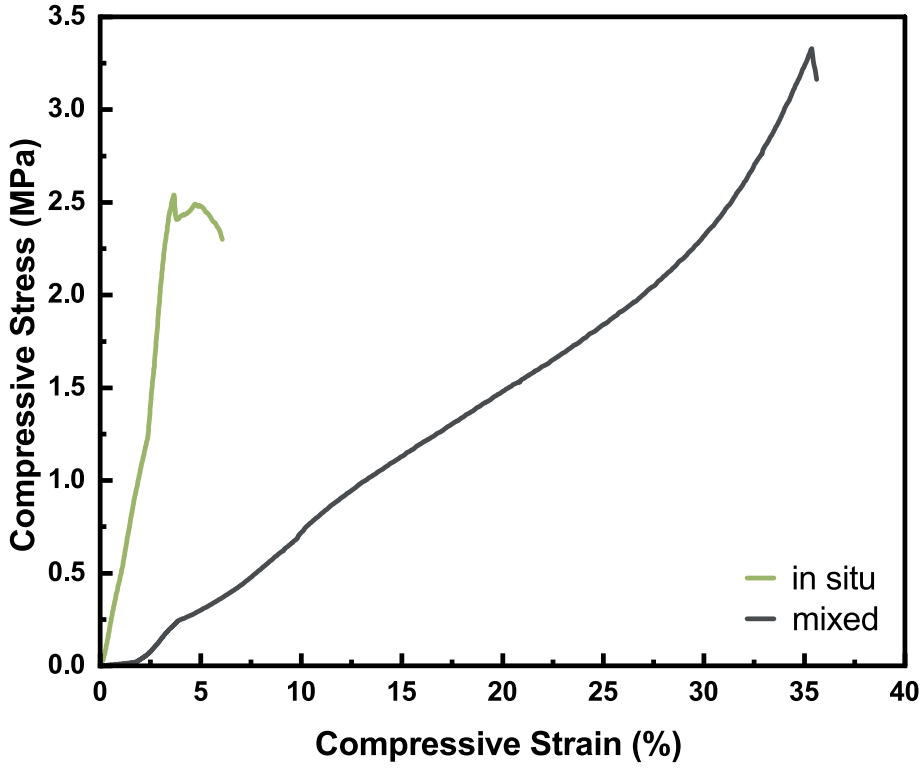
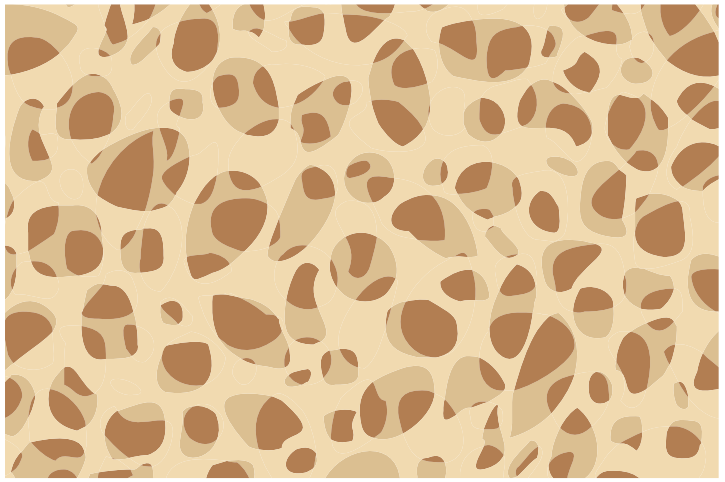
Mechanical Behavior of Biomineralized Composite

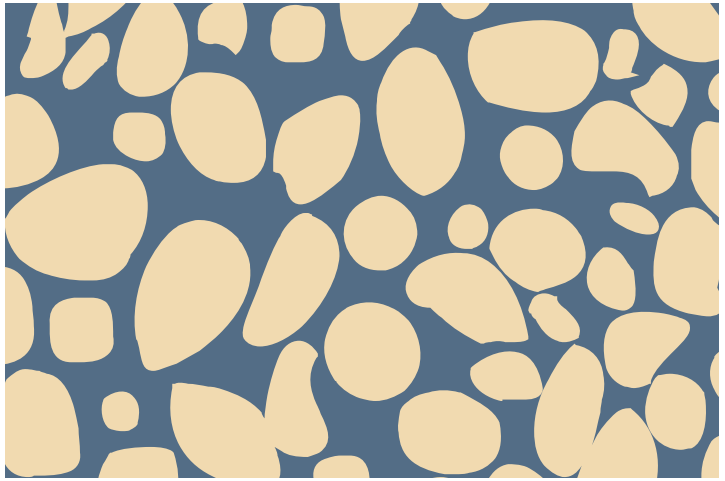


Mechanical integrity is granted by mineral bridges

Biomineralized



Pre-mixed



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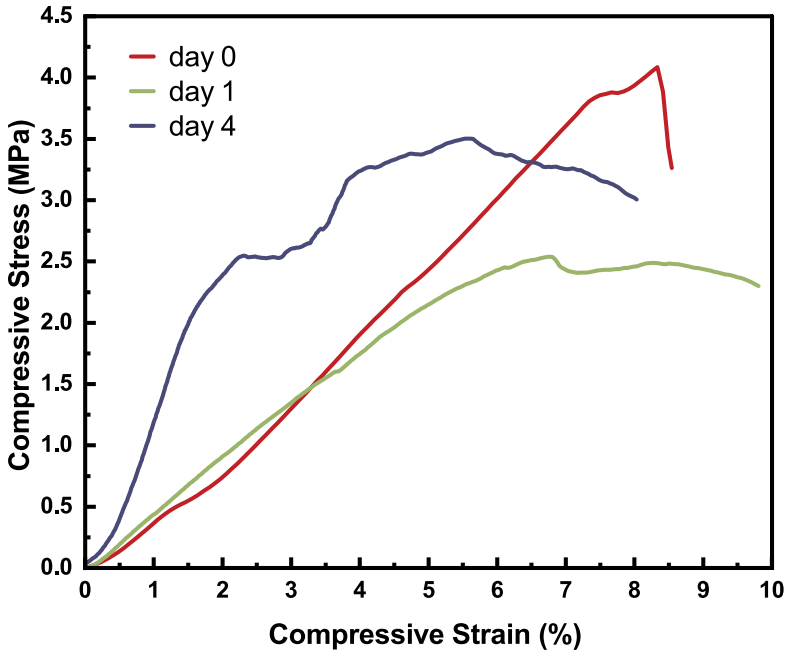
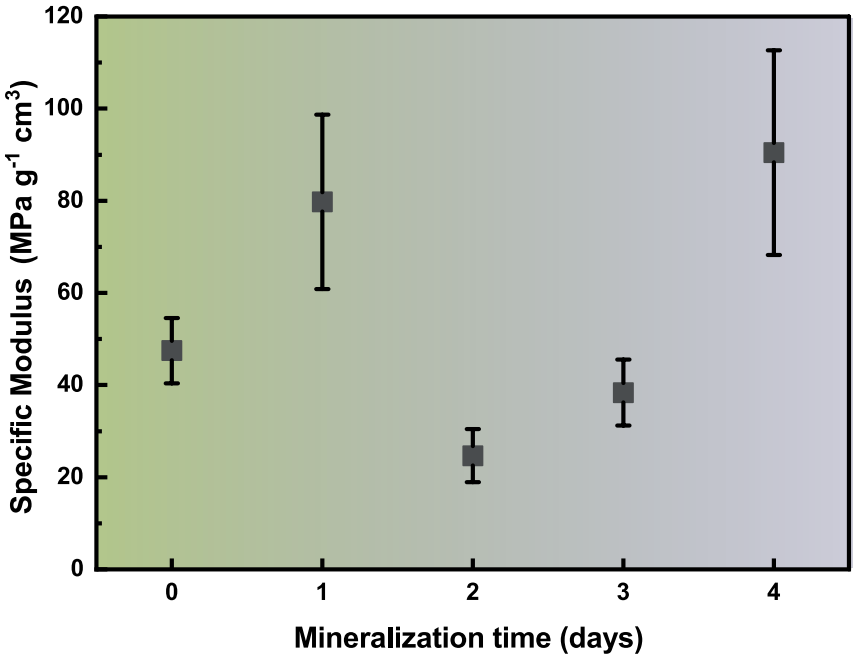
Mechanical Behavior of Biomineralized Composite

Matteo Hirsch



pH 7 → pH 10



Alkaline pH affects gelatin network stability

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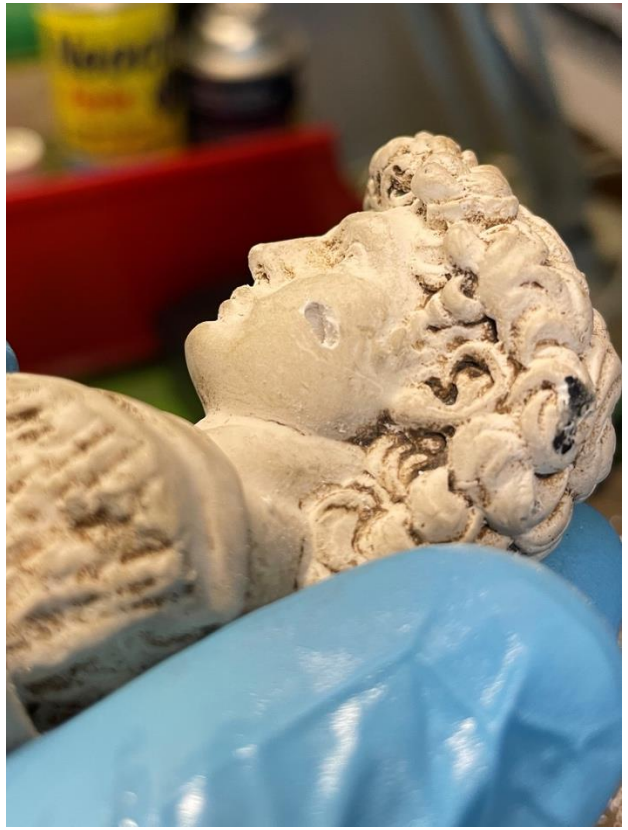
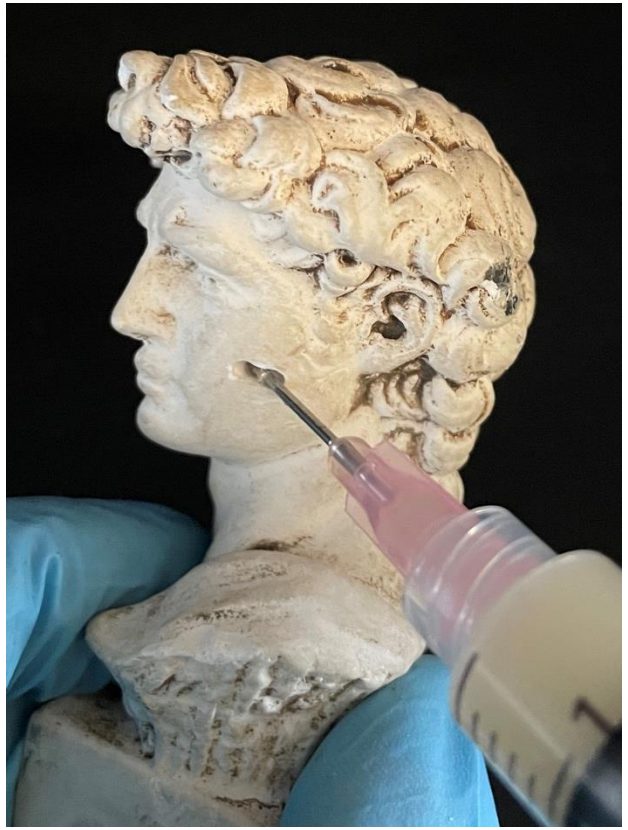
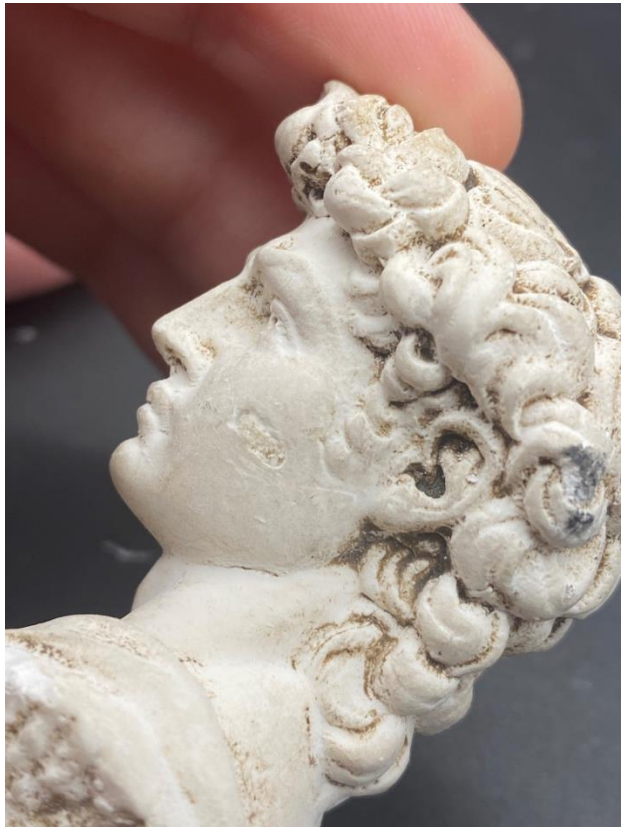
Art Restoration







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Press Release

EPFL About Education Research Innovation Schools Campus

Help and support: current initiatives

3D printing with bacteria-loaded ink produces bone-like composites

News › Research

EPFL researchers have published a method for 3D-printing an ink that contains calcium carbonate-producing bacteria. The 3D-printed mineralized bio-composite is unprecedently strong, light, and environmentally friendly, with a range of applications from art to biomedicine.

Read more ›

EPFL **Press Release**

MIKE OLSON NOV 1, 2011 12:30 PM

Appetite for Art: Restoring Ancient Works With Hungry Bacteria

Fire, glue, and salt blooms have wreaked havoc on some of Spain's 17th-century masterpieces. It's up to bacteria to undo the damage.

The latest technology in art restoration? Bacteria

Ben Wedeman, CNN and Jacqui Palumbo, CNN

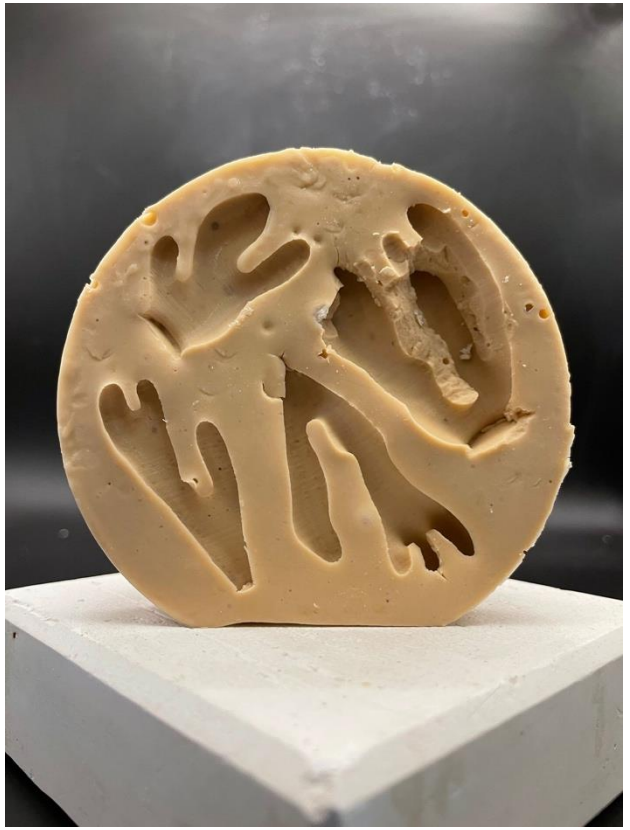
3 minute read · Published 5:45 AM EDT, Tue October 26, 2021

Send in the Bugs. The Michelangelos Need Cleaning.

Last fall, with the Medici Chapel in Florence operating on reduced hours because of Covid-19, scientists and restorers completed a secret experiment: They unleashed grime-eating bacteria on the artist's masterpiece marbles.

Share full article

Marine Reef Remediation



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SCIENCE NEWS

Scientists are trying to save coral reefs. Here's what's working.

Without these interventions, scientists say the Earth's coral reefs as we know them could disappear before the next century.

By Sarah Gibbens

June 4, 2020 • 9 min read