2016 MIT Research & Development Conference: Track 2: Bioinspired Materials
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Biomanufacturing

Markus J. Buehler

McAfee Professor of Engineering, MIT

Department Head, Civil and Environmental Engineering
Director & PI, Laboratory for Atomistic and Molecular Mechanics
Massachusetts Institute of Technology

E-mail: mbuehler@MIT.EDU

URL: http://web.mit.edu/mbuehler/www/

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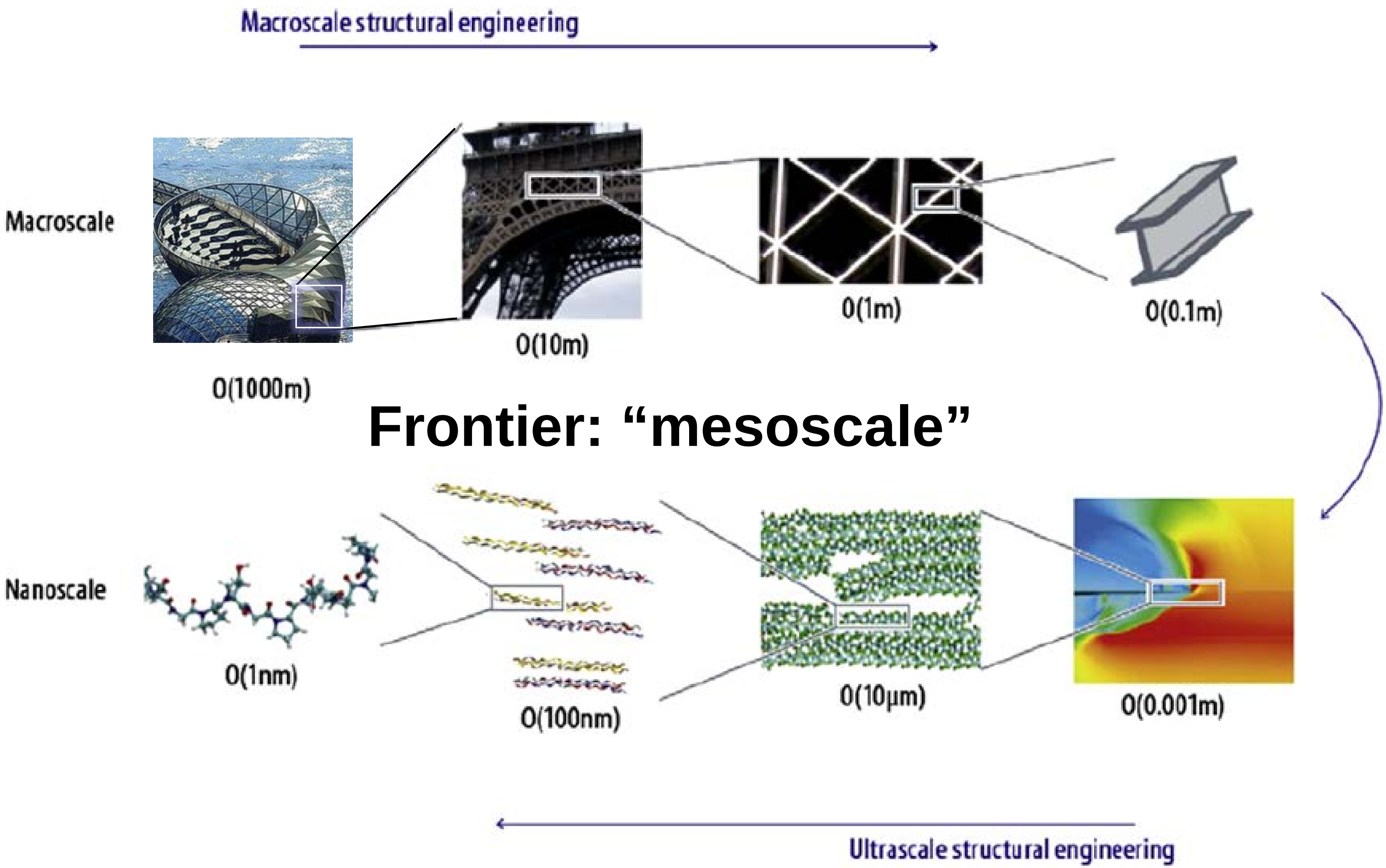
Civil and Environmental Engineering

Engineering design at all scales: Materiomics



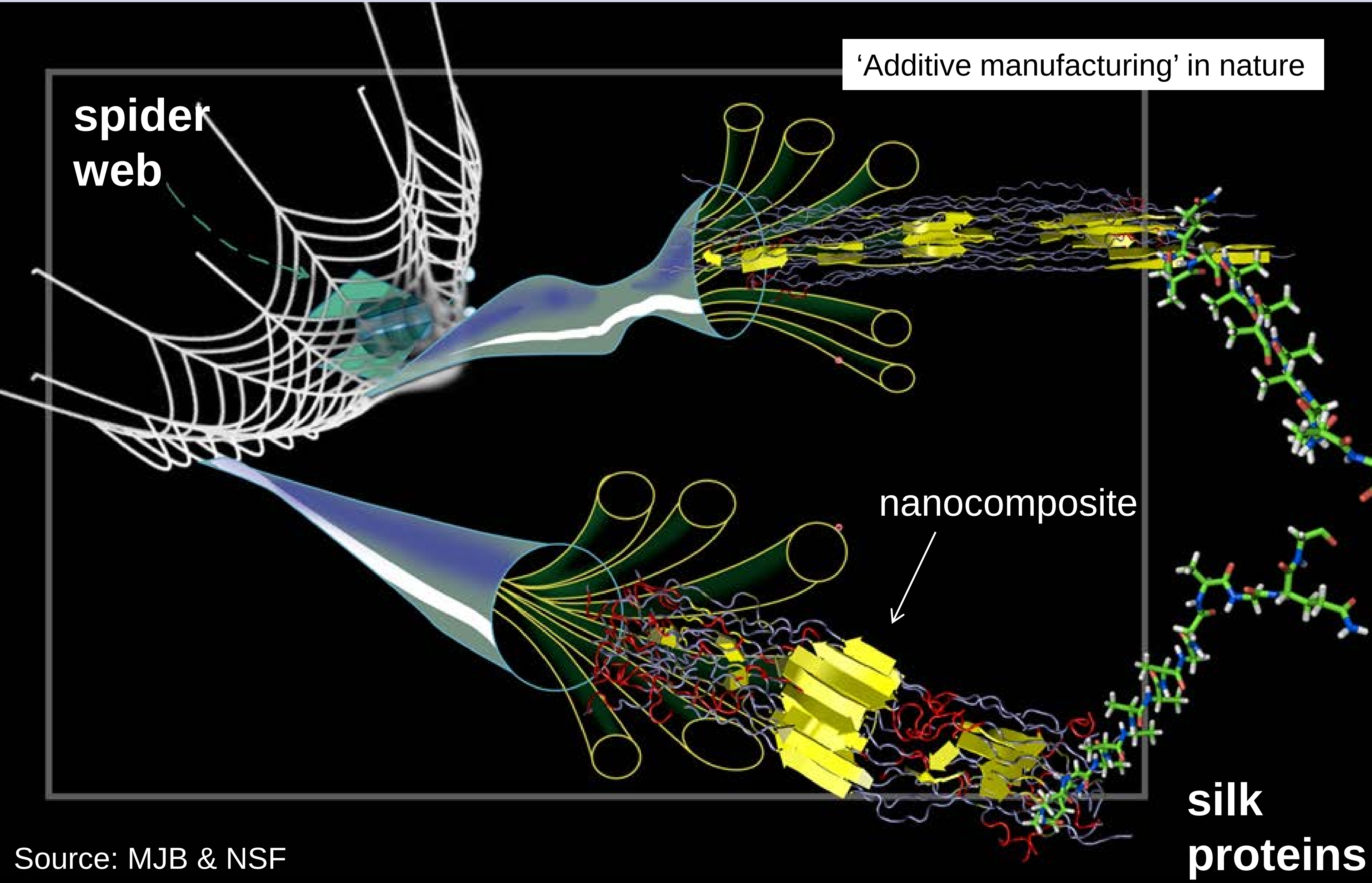
Ackbarow, Buehler *et al., Materials Today*, 2007


Orb web
Francesco Tomasinelli and Emanuele Biggi

Cocoon

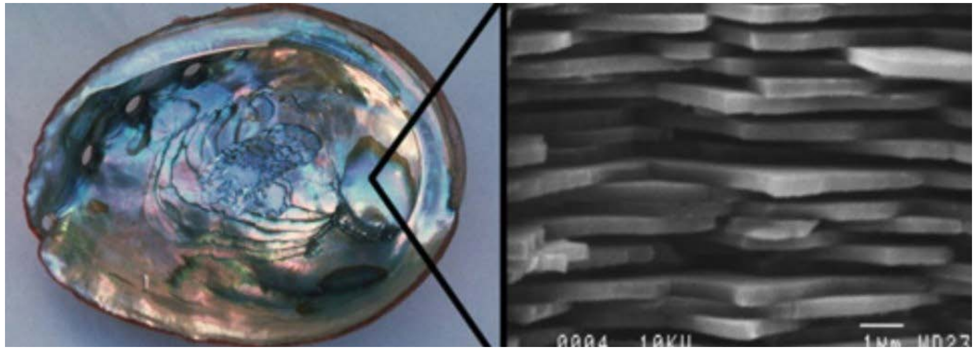

Mussel adhesion
(underwater, any
surface)

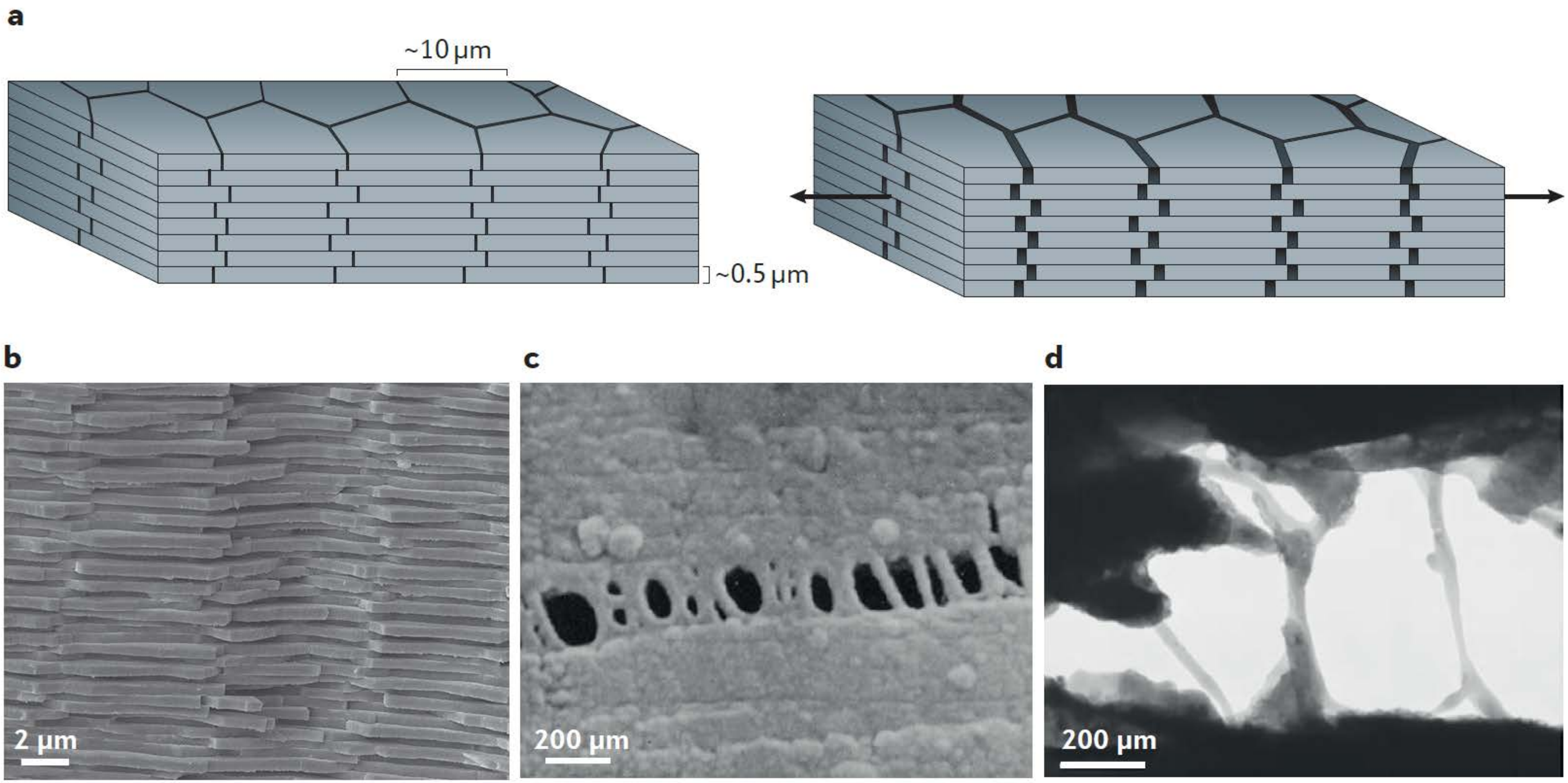
Steel: strength ~1 GPa: strong bonds
Spider silk: strength: ~1-2 GPa & 60% strain @ failure extreme toughness
weak bonds; made @ room temperature via self-assembly



Source: MJB & NSF

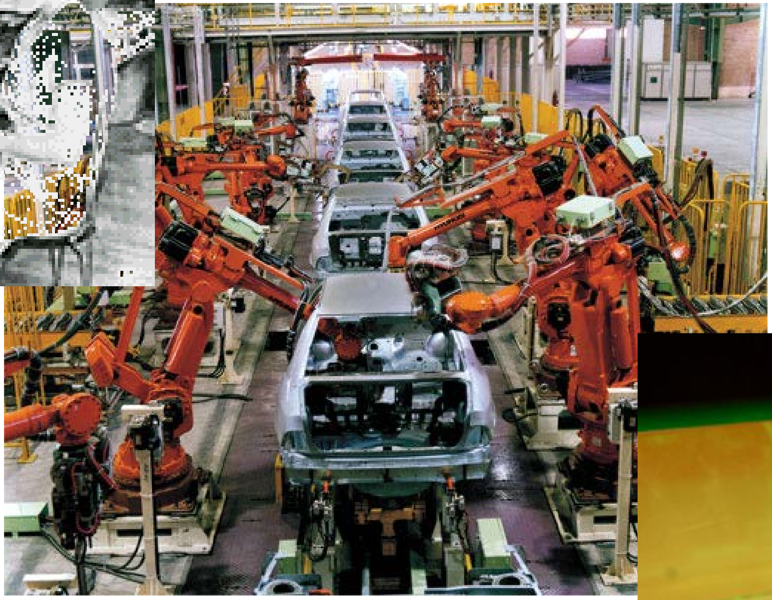
Nacre



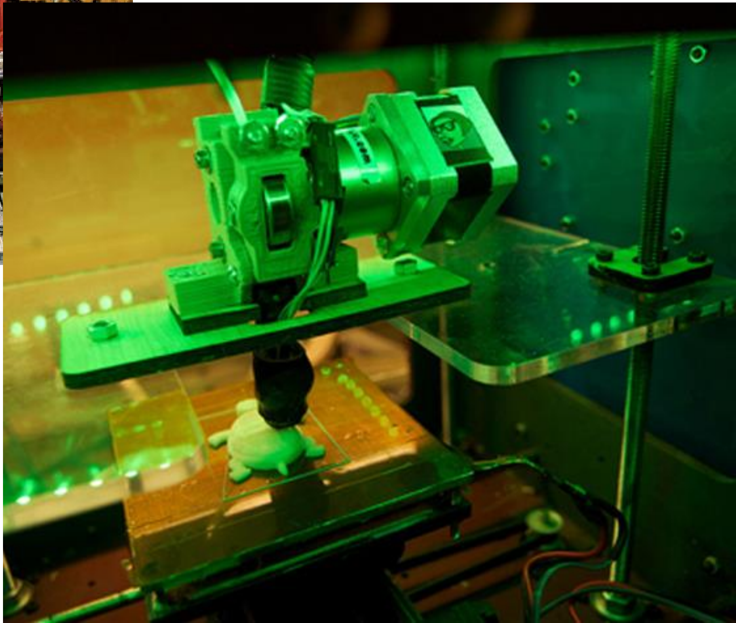


How we make stuff

1900s



1990s



2020
Grow materials (self-assemble)
Print things (3D printing)

Top-down vs. bottom-up

Material Design

Conventional: **"Top-down approach"**

- Requires many different raw materials
- Limited structural control & flexibility

Van Vliet, Yip, Buehler, Ulm *et al.*, *MRS Bulletin*, 2012

New: "Bottom-up approach"

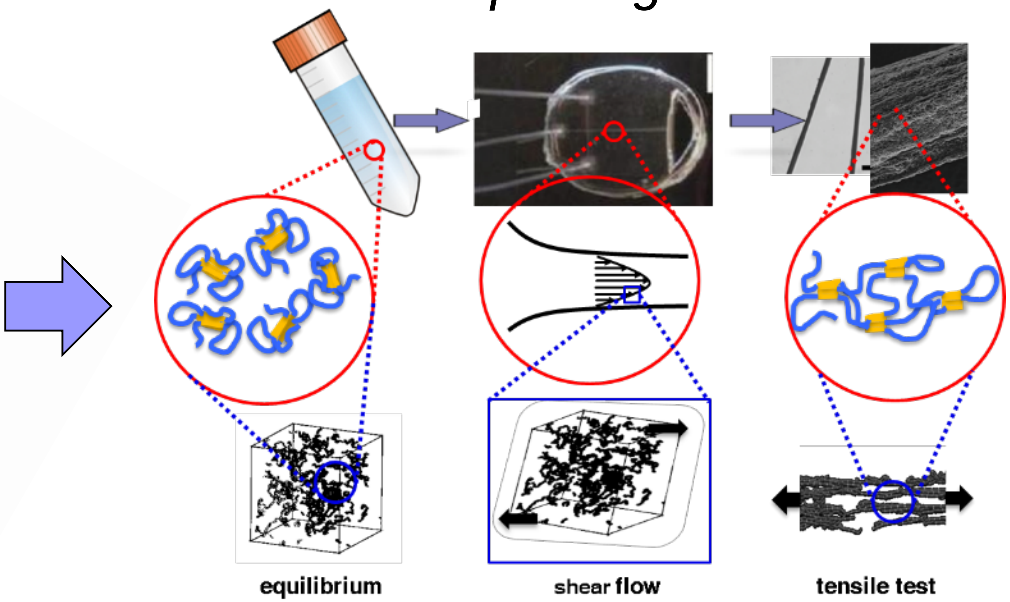
- Few raw materials
- Enhanced flexibility through structure
- Integration of material synthesis with manufacturing of product (system perspective)
- Bioinspired

A new paradigm of material design

“bottom-up approach” – example: spider silk, self-assembled solid, stronger than steel

processing: spinning

DNA



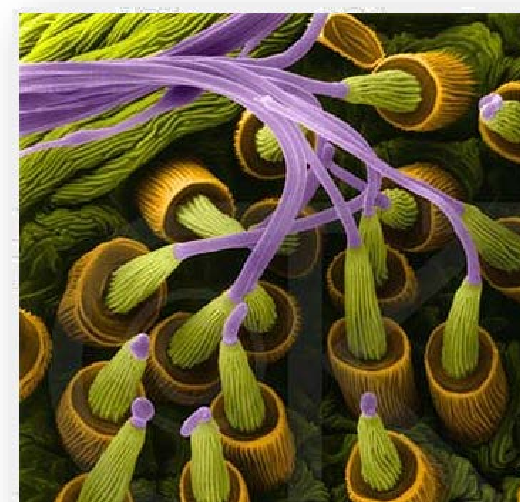
4 ‘letters’
ACGT

protein

20 building blocks
(amino acids)

material/ tissue

Dennis Kunel



(spider) silk spinning
liquid to solid

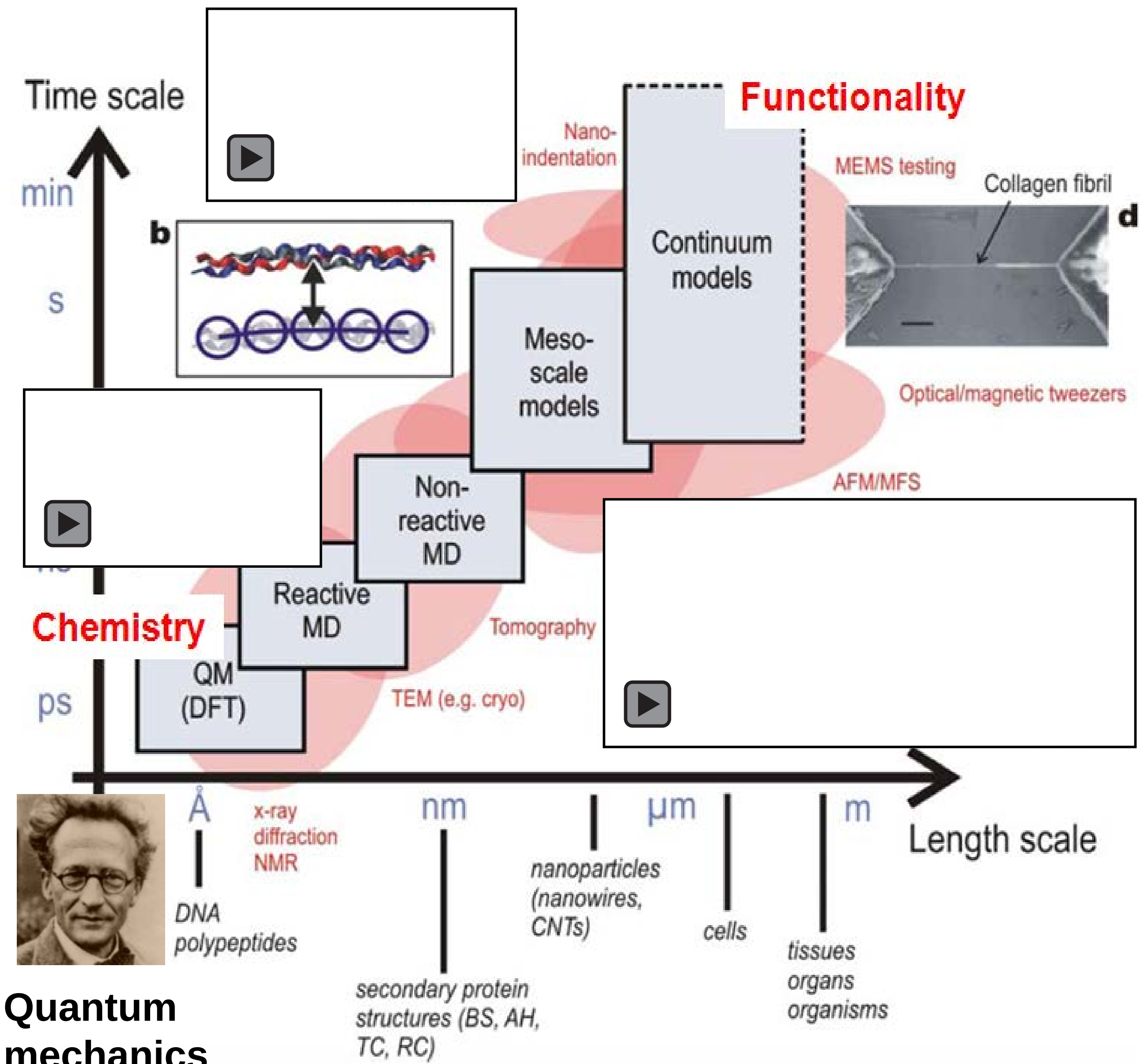
M. Buehler *et al., Nano Letters*, 2011; *Nature*, 2012; Kaplan, Buehler, Wong, *et al.*, 2012

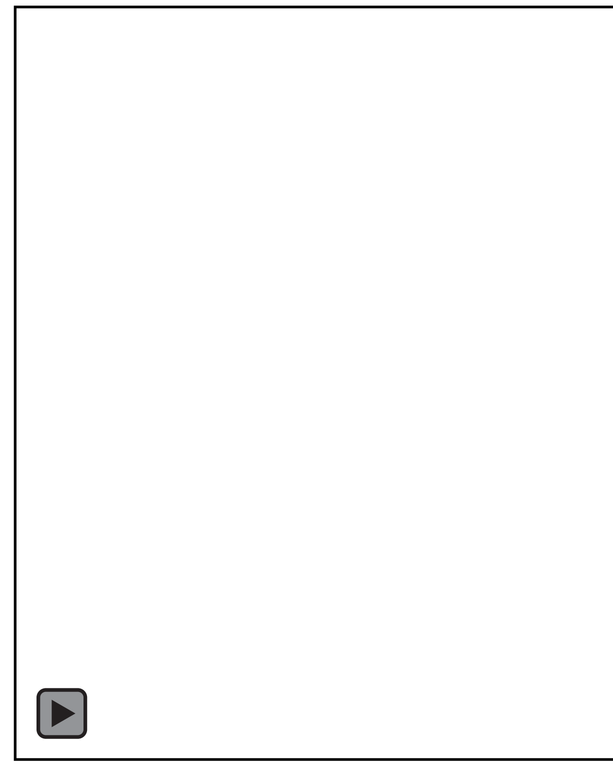
MIT/Harvard ‘synthetic spider web’

Z. Qin, J. Lewis, M. Buehler *et al.*, *Nature Comm*, 2015

Integration of experiment and computation

Connecting the virtual to the physical world





Buehler *et al.*, *Nature Materials*, 2009;. Z. Qin *et al.*, 2010, 2012

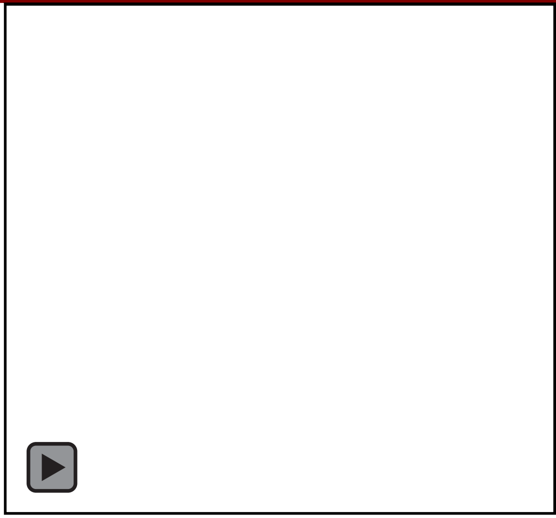
Structure prediction and functional properties

Genetic level (DNA)

…GGLGGQGAGAA
AAAAGGAGQG …

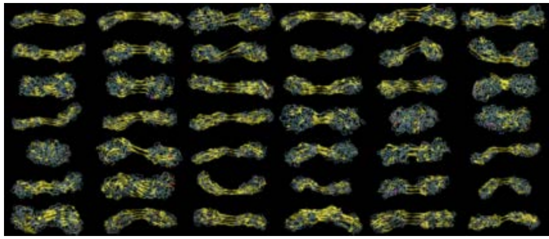
Amino acid sequence

Replica Exchange Simulations

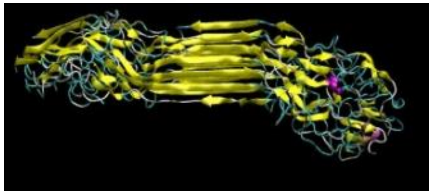


Ensemble of final structures

Folding—structure

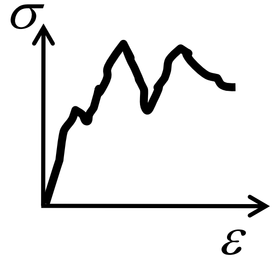


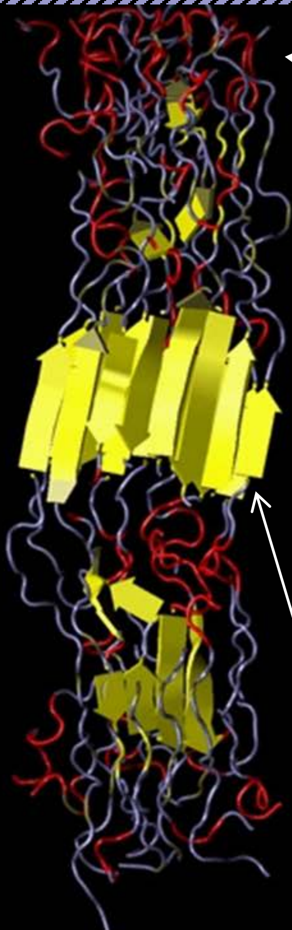
Validation (experimental results)



Mechanical characterization (multiscale)

Mechanics (functionality)

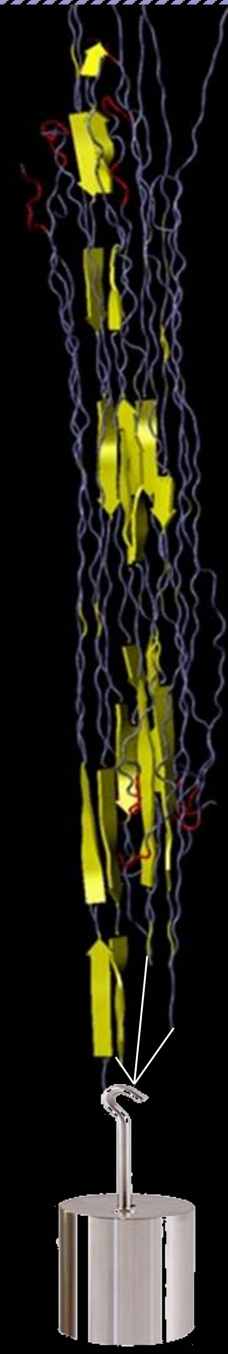




hydrophilic
(mix w/ water)
= **B**

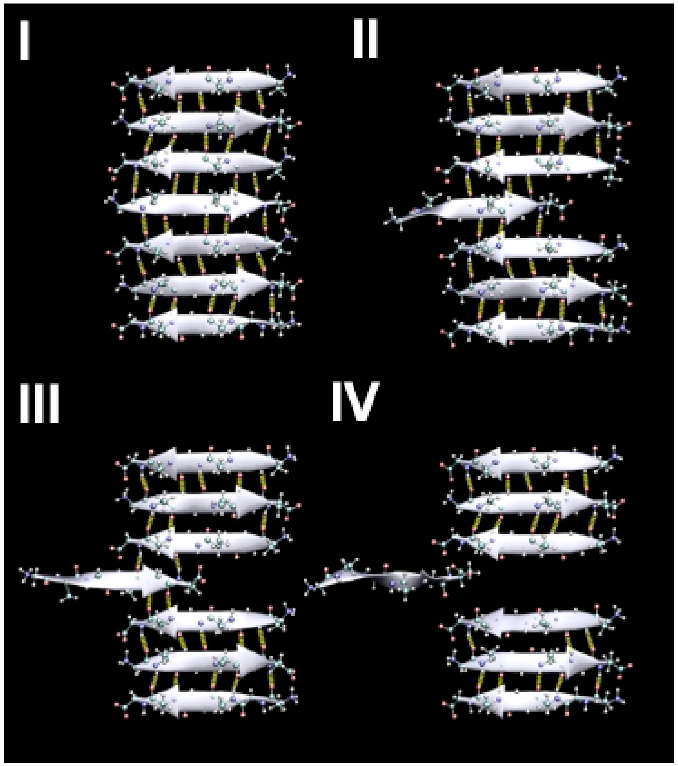
~2-3 nm
(nanocrystal)

hydrophobic,
form crystals
(don't mix w/
water) = **A**

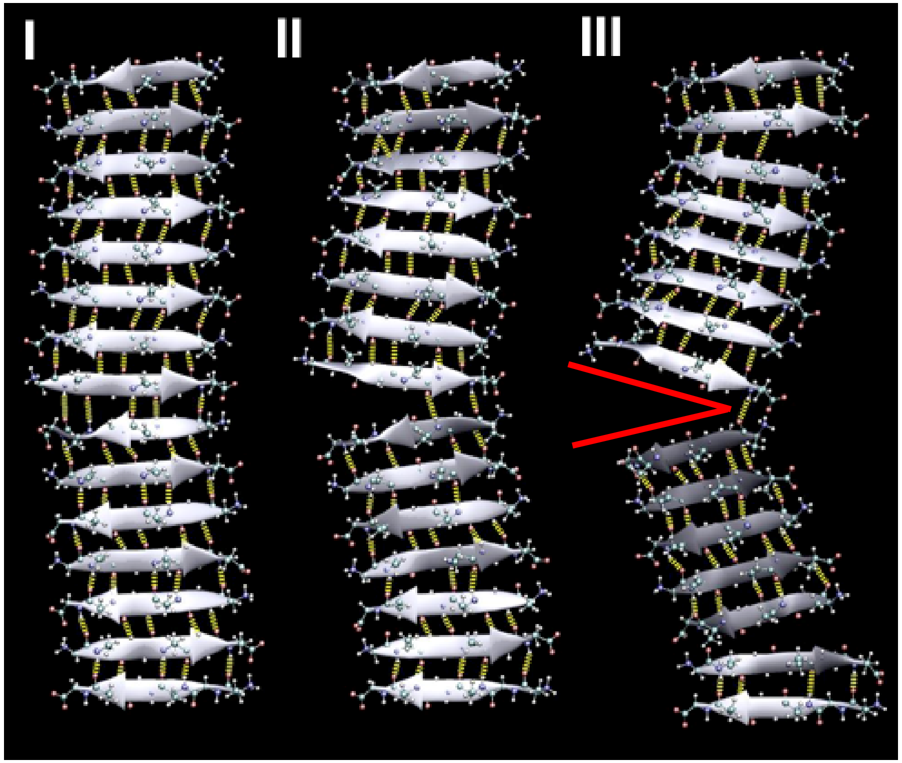


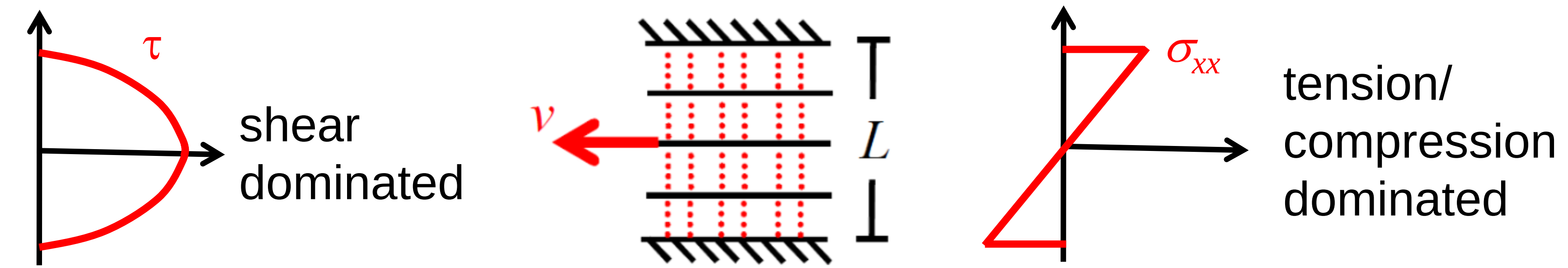
Size effects in silk nanocrystals

pull-out setup (small system)



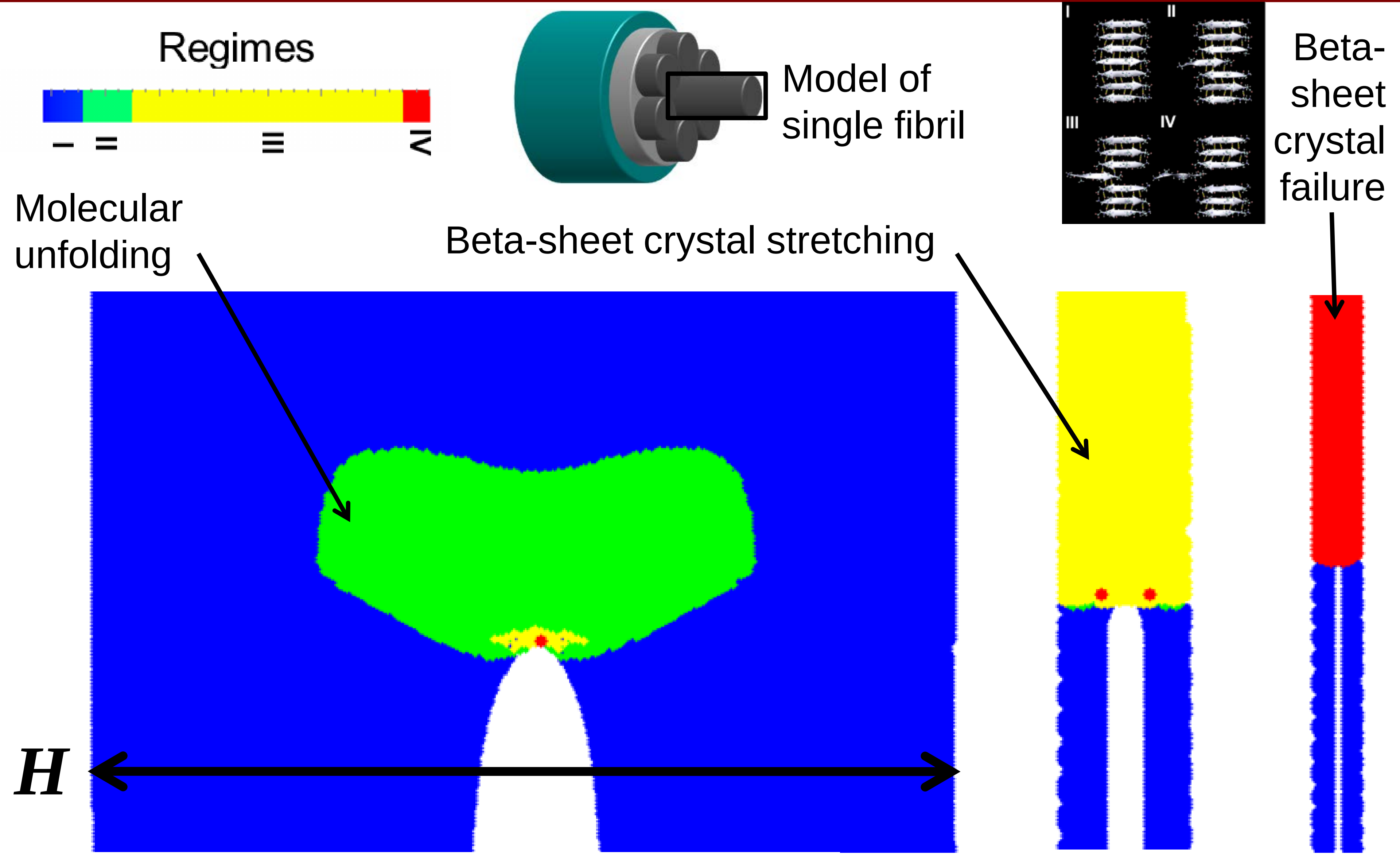
pull-out setup (large system)





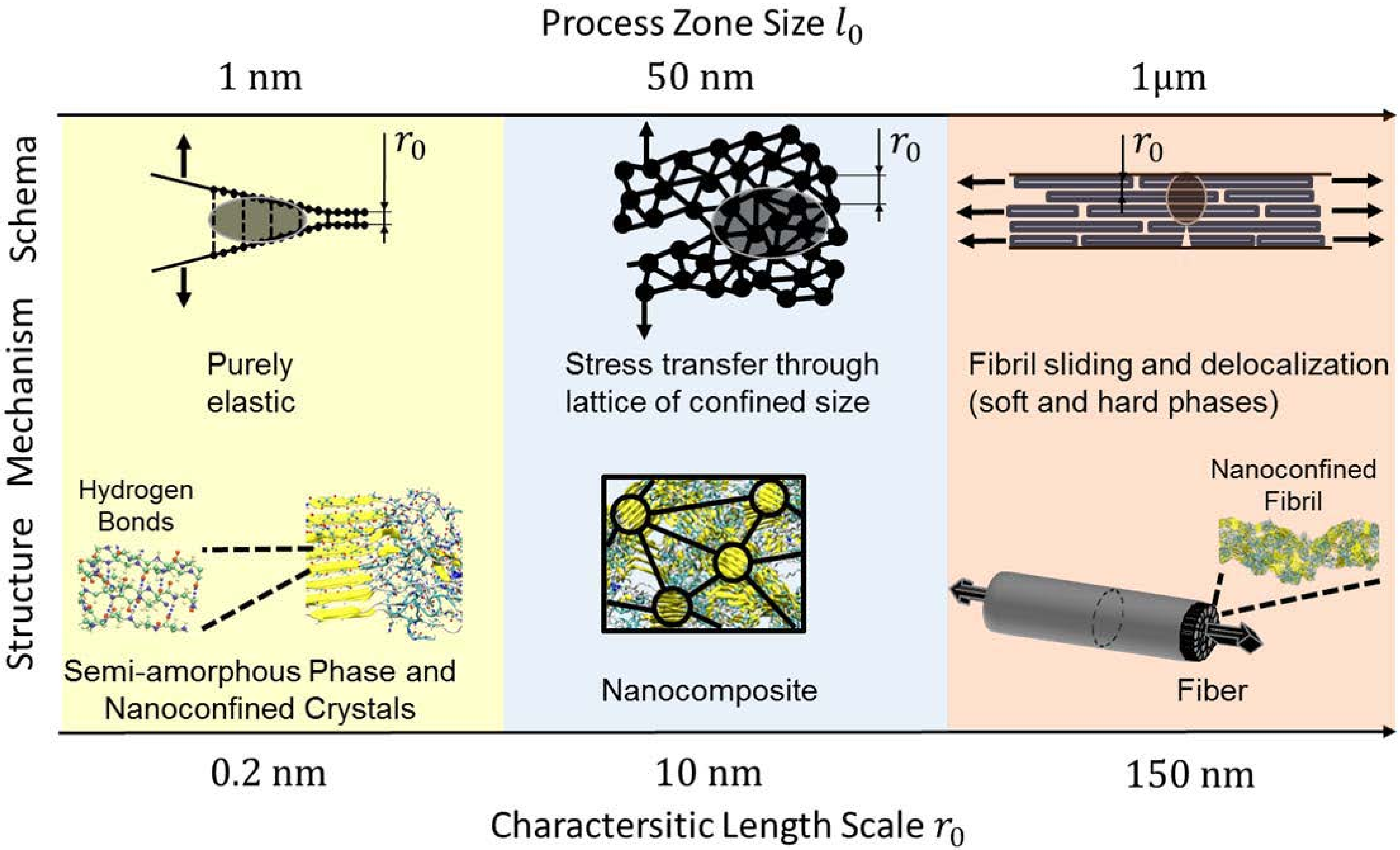
Keten, Xu, Ihle, Buehler, *Nature Materials,* 2010

Mechanism of upscaling



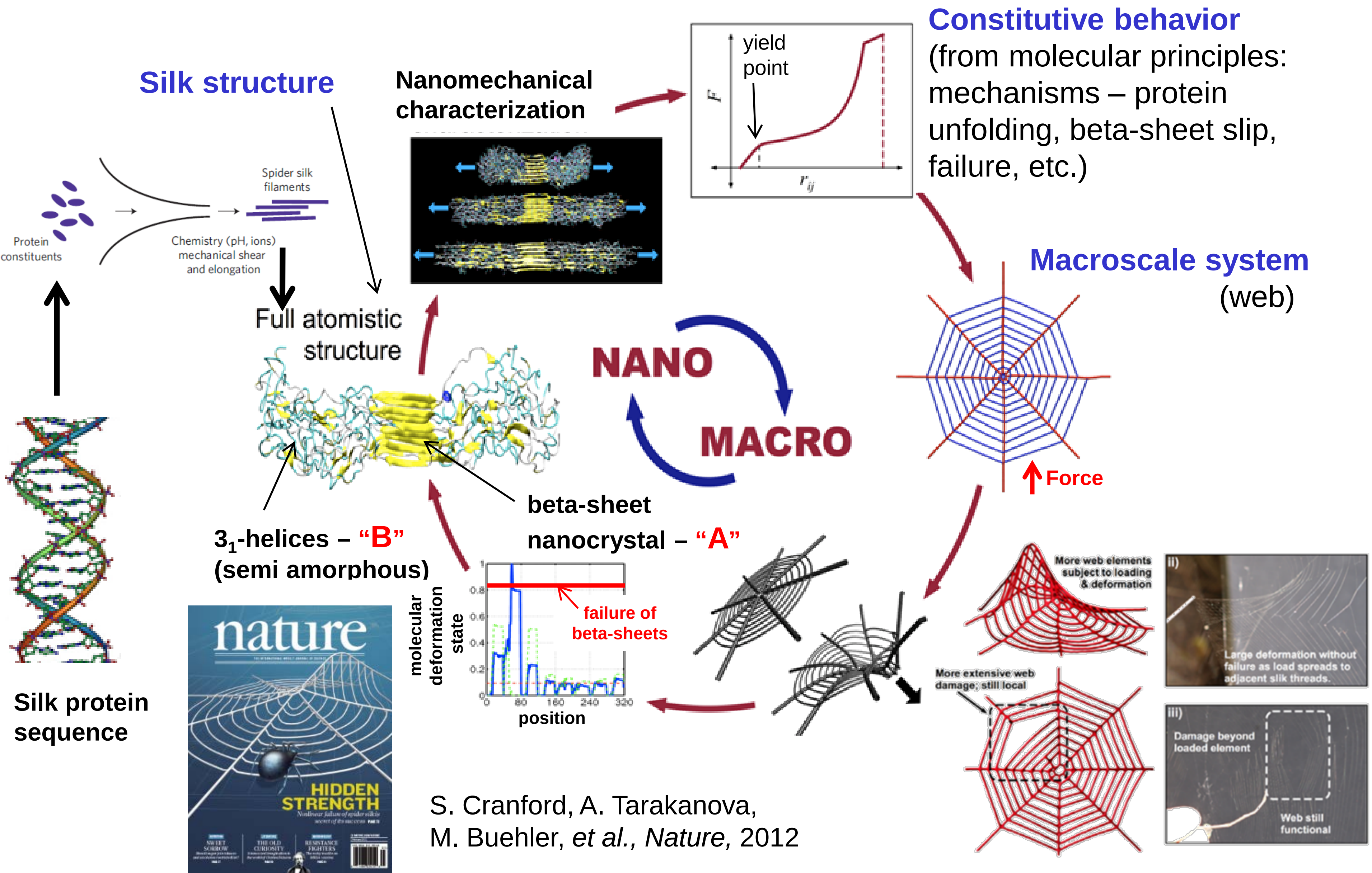
T. Giesa, M. Arslan, M. Buehler, *Nano Letters,* 2011

Hierarchical upscaling



T. Giesa, et al., Adv. Mater., 2014

Mechanics of spider webs

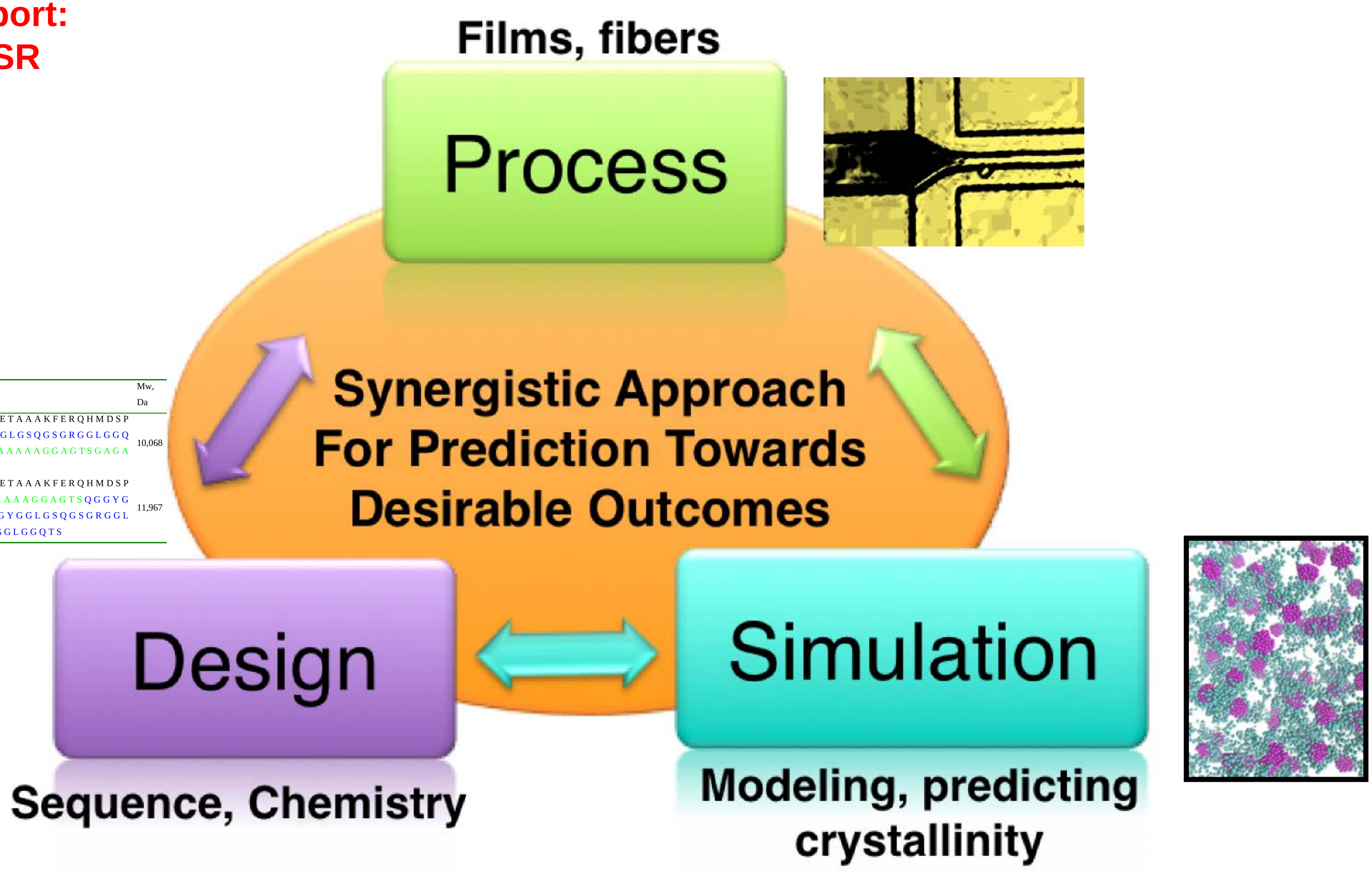


S. Cranford, A. Tarakanova, M. Buehler, *et al.*, *Nature*, 2012

Connecting design, process, simulation

NIH U01
Other support:
ONR, AFOSR

Joyce Wong (Boston University)



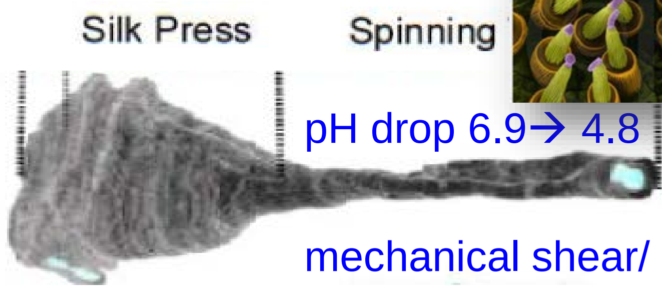
Code	Spider silk-like block copolymers	Mw, Da
HBA_3	M H H H H H H S S G L V P R G S G M K E T A A A K F E R Q H M D S P D L G T D D D D K A M A A S Q G G Y G G L G S Q G S G R G G L G G Q T S G A G A A A A A G G A G T S G A G A A A A A G G A G T S G A G A A A A A G G A G T S	10,068
HAB_3	M H H H H H H S S G L V P R G S G M K E T A A A K F E R Q H M D S P D L G T D D D D K A M A A S G A G A A A A A G G A G T S Q G G Y G G L G S Q G S G R G G L G G Q T S Q G G Y G G L G S Q G S G R G G L G G Q T S Q G G Y G G L G S Q G S G R G G L G G Q T S	11,967

David L. Kaplan (Tufts University)

Markus J. Buehler (MIT)

Mimicking a spider's spinning duct

Spider's spinning duct

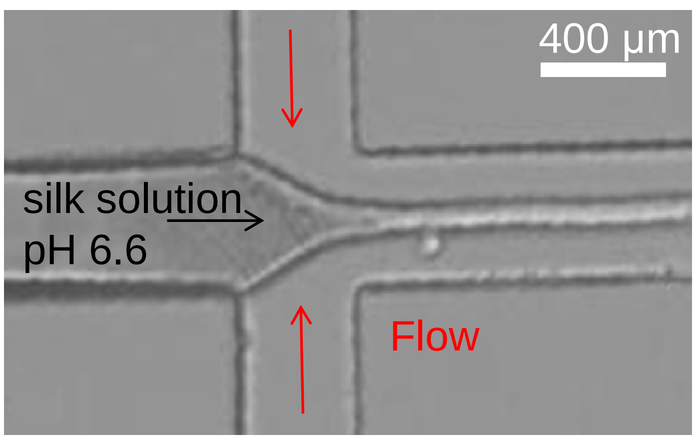


pH drop 6.9→ 4.8

mechanical shear/
elongational flow

protein dope → semicrystalline fiber

Microfluidic Spinning



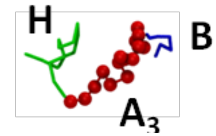
fiber

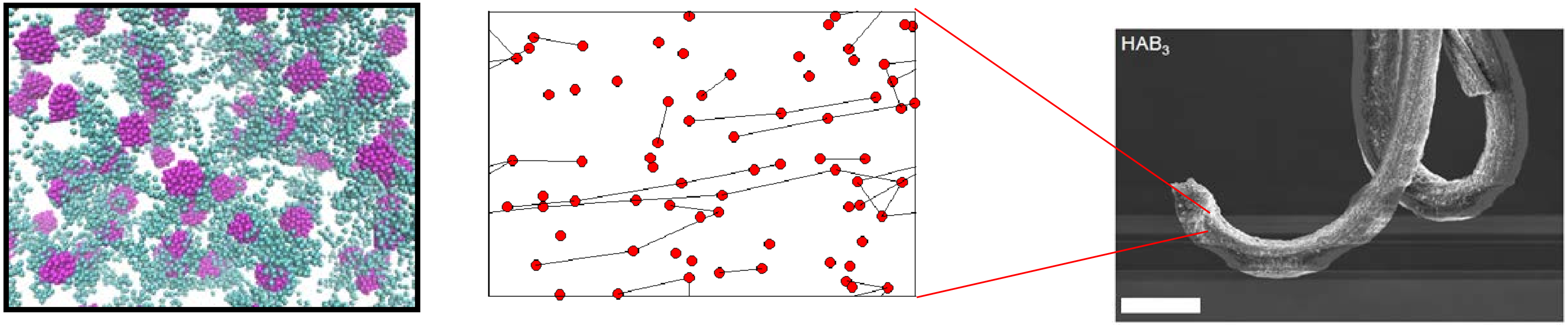
Enable to test small volume
& to tune processing conditions

Microscopic insight from molecular simulation

a

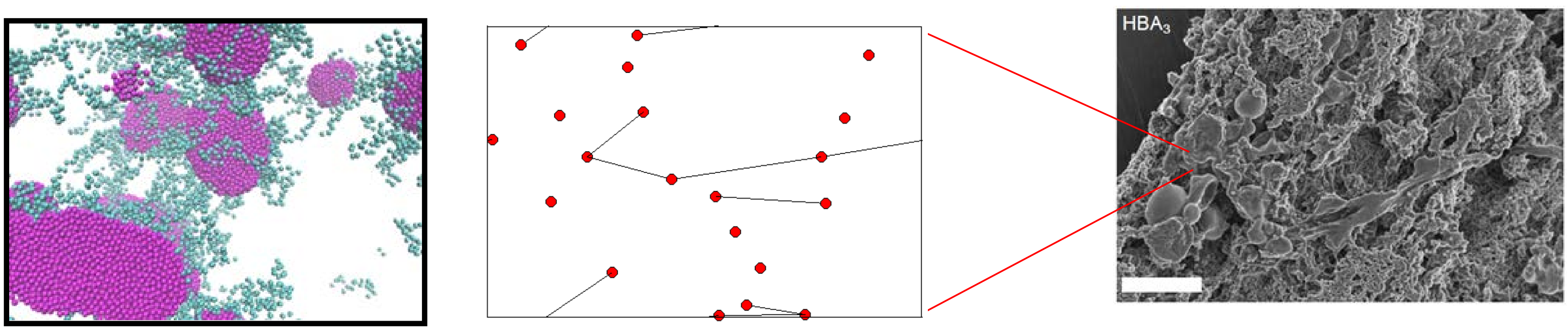
b





HAB3 + RSF, Homogeneous Material → forms fiber, but

Some connectivity → sustains tensile load

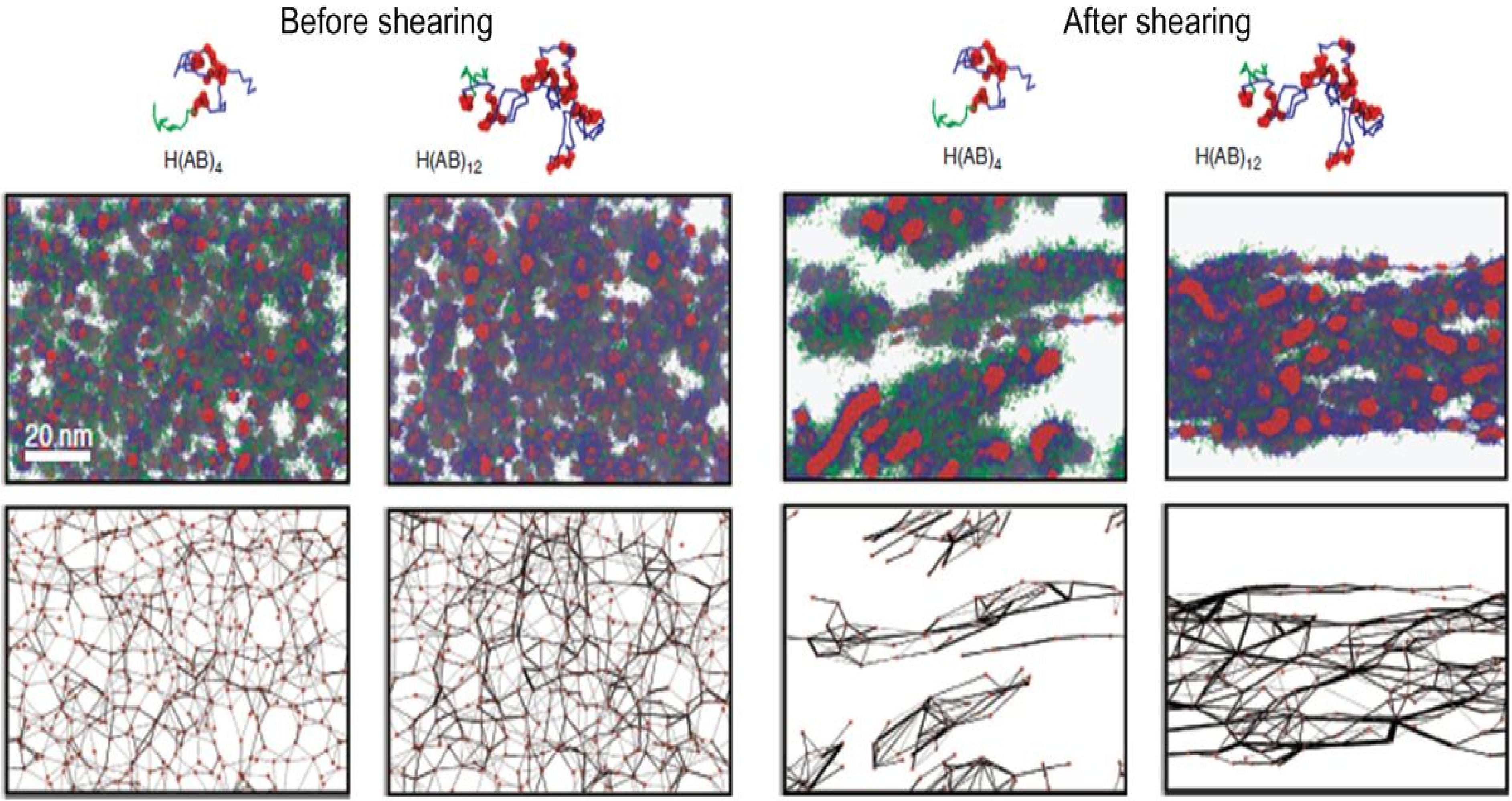


HBA3 + RSF, Inhomogeneous Aggregates → forms globular aggregates,

Very poor connectivity → breaks by tiny agitation

Ling, Ryu, Gronau, Kaplan, Wong, Buehler *et al.*, Nature Comm. 2015

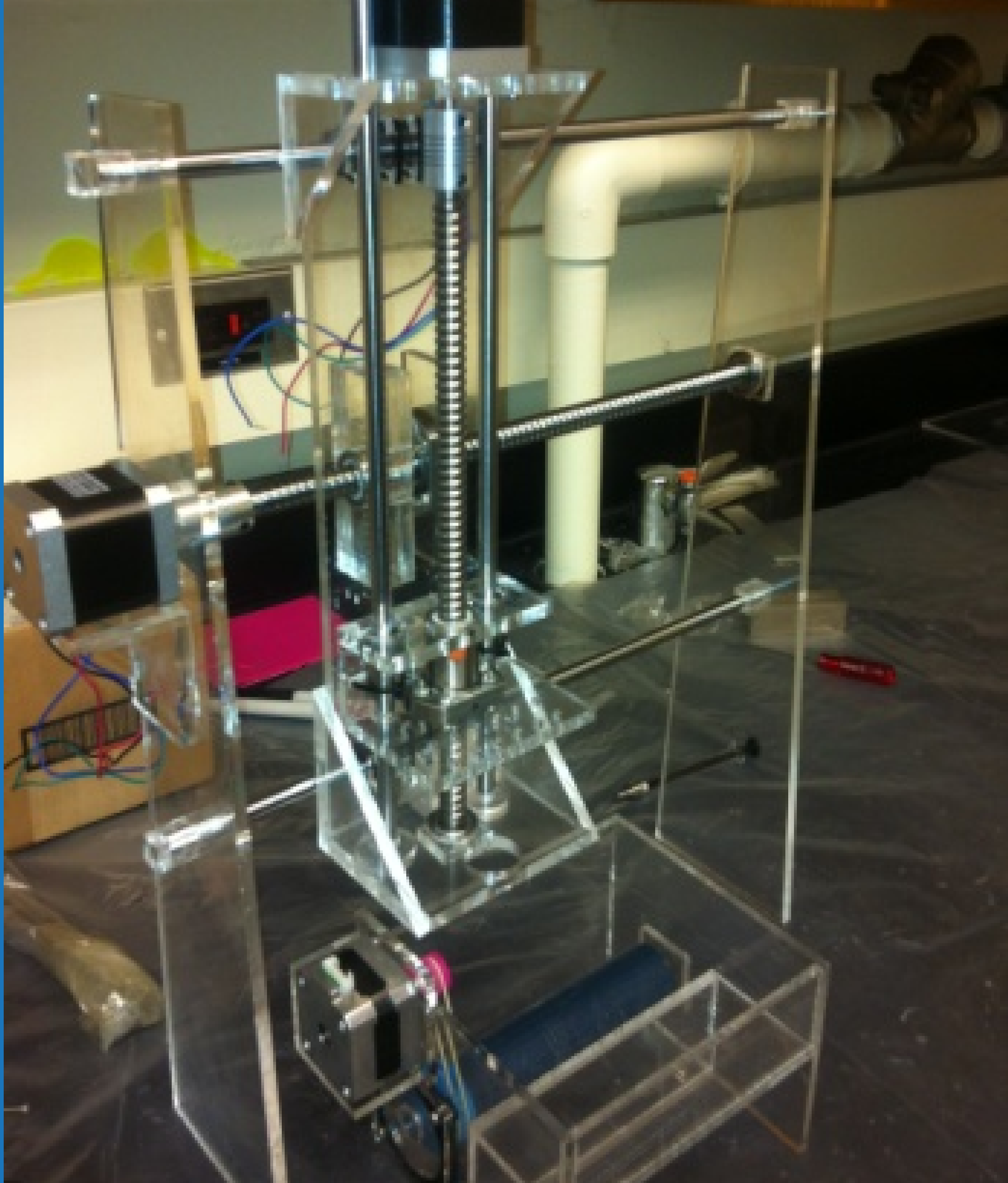
Network evolution after equilibration and shear



Ling, Ryu, Gronau, Kaplan, Wong, Buehler *et al.*, Nature Comm. 2015

Custom-built 3D printer

Connect modeling/simulation, optimization, design to making real physical samples



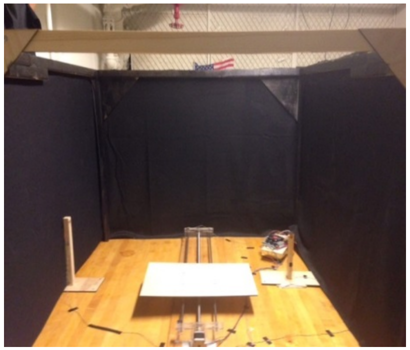
3D printed ‘synthetic spider web’

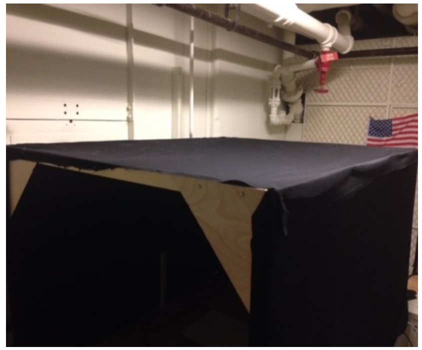
Z. Qin, B, Compton, J. Lewis, M. Buehler, *Nature Comm.*, 2015

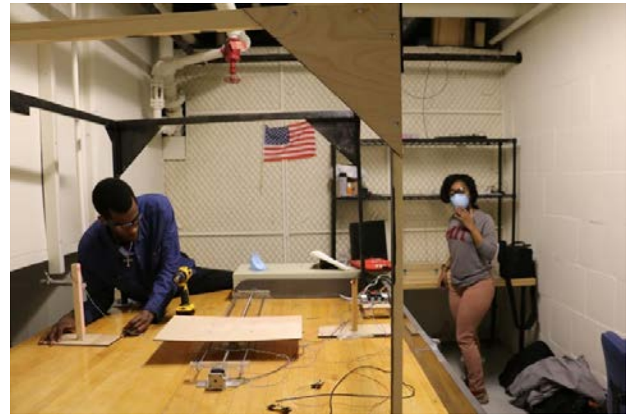
Tomás Saraceno/CAST

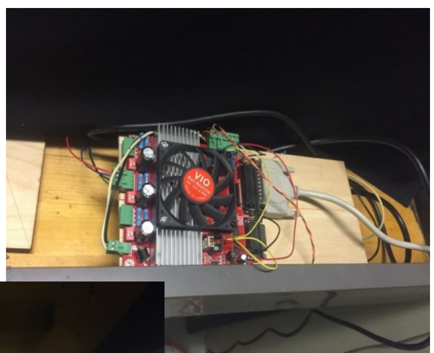
3D webs

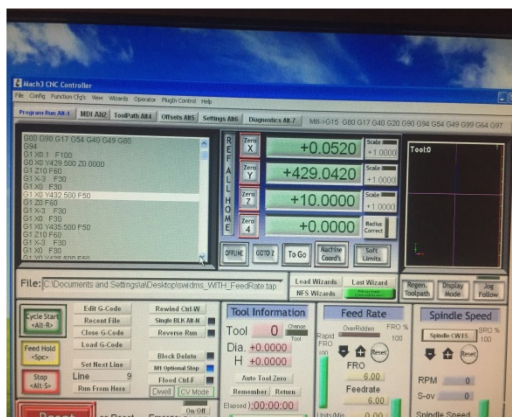
Characterization method to scan complex 3D web structures

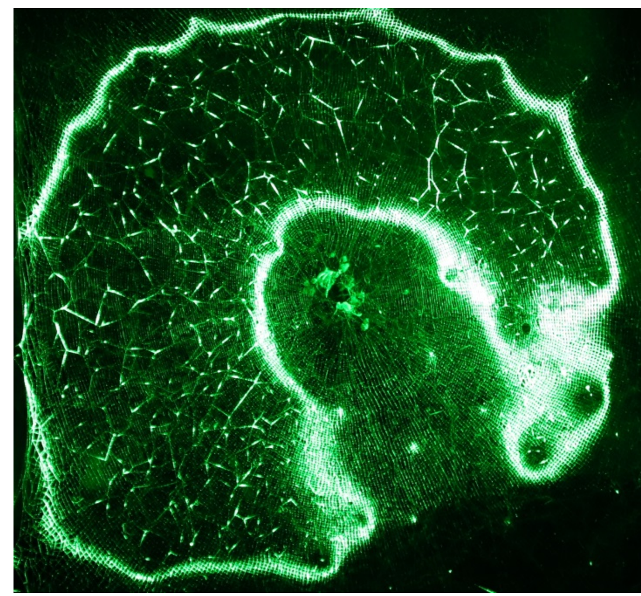








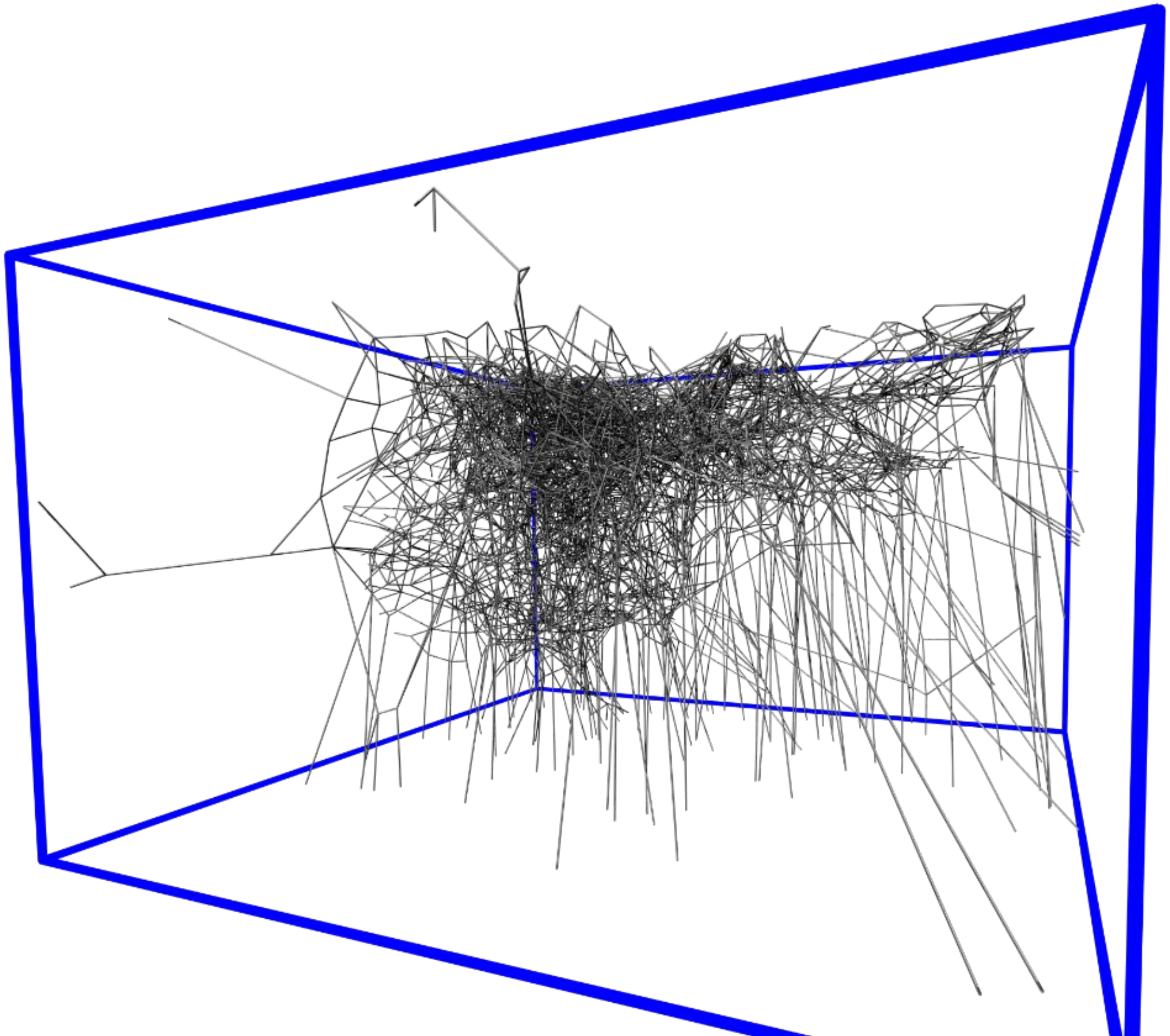




Civil and Environmental Engineering

Z. Qin, S. Nyambo, B. Ndengeyingoma, Y. Wangare, M. Buehler

Computer model

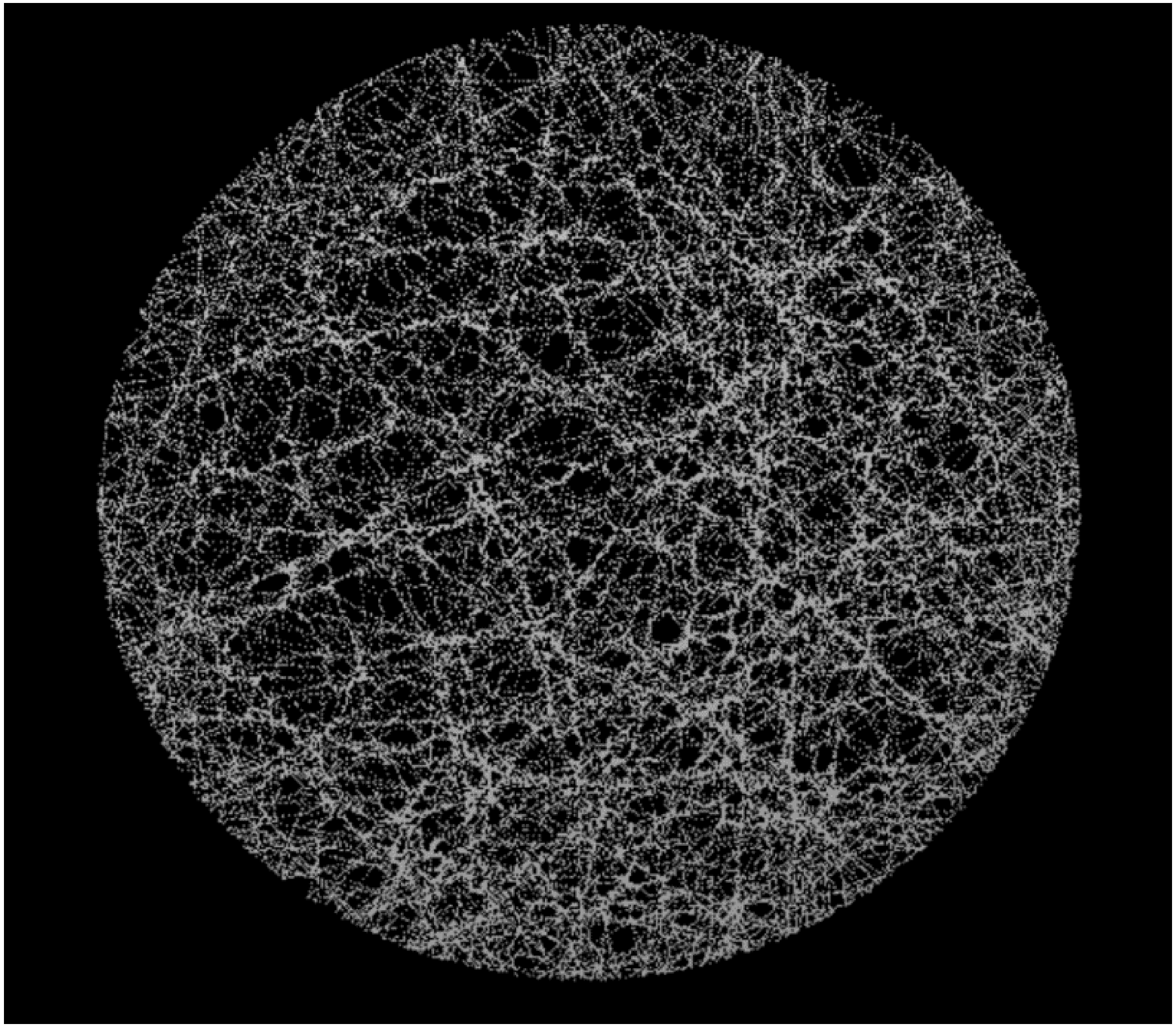



Silk cocoons…

Design of the web structure (cont'd)

I. Su, Z. Qin, M. Buehler

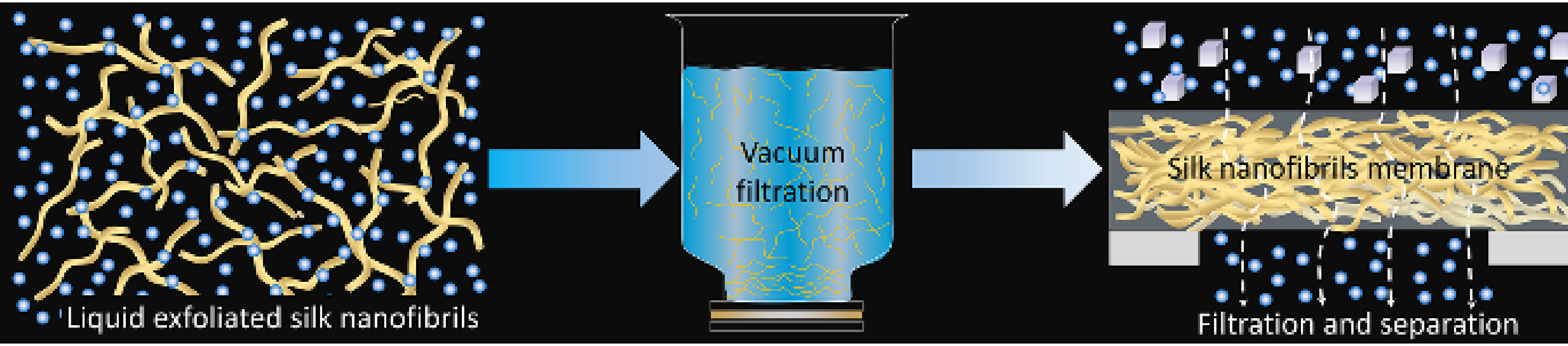
2D silk structures, membranes



Can we scale this down?

Silk-inspired materials and devices

Silk-based filtration material

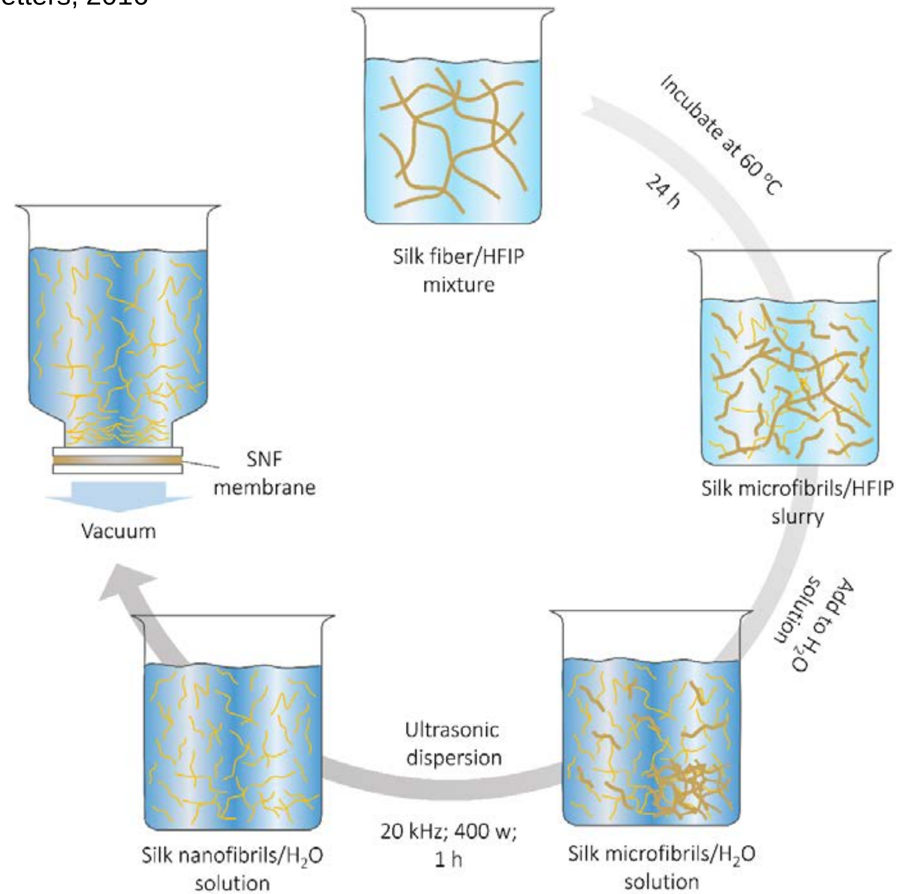


Ultrathin filtration membrane prepared from silk nanofibrils (SNFs), directly exfoliated from natural *Bombyx mori* silk fibers to retain structure and physical properties

Ling, Jin, Kaplan, Buehler et al., Nano Letters, 2016

Ling, Jin, Kaplan, Buehler et al., Nano Letters, 2016

Cost ~\$0.05-\$0.51 compared with \$1.20 per piece of commercial filtration membrane

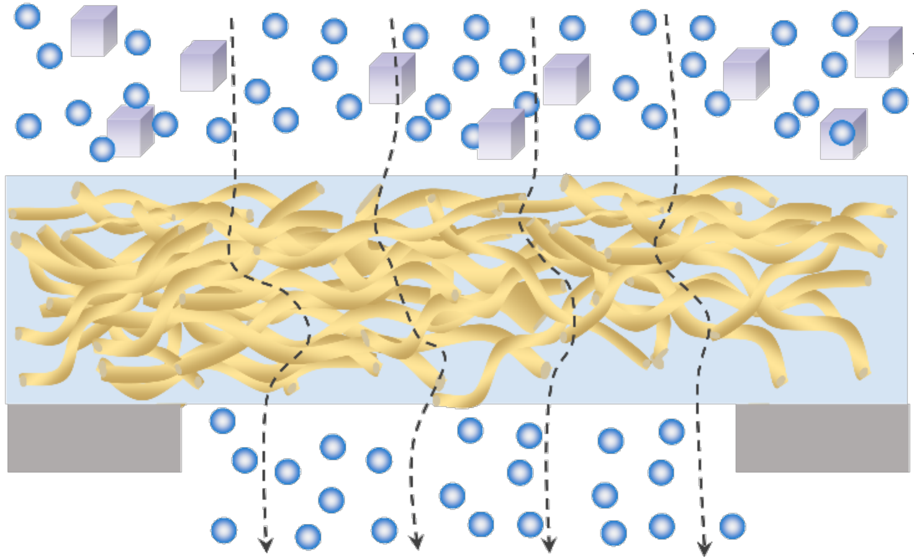


HFIP=hexafluoro-2-propanol

- **Schematic of the process used to design ultrathin SNF membranes** . **Step 1**, silk fiber immersed in HFIP with a weight ratio of 1:30 and incubated at 60°C for 24 h to obtain silk fiber/SMF slurries. **Step 2**, the dried silk fiber slurries transferred to H_2O solution and precipitates removed. **Step 3**, SMF dispersion treated by ultrasound to extract SNFs. **Step 4**, SNF dispersion assembled to ultrathin SNF membranes *via* vacuum filtration.

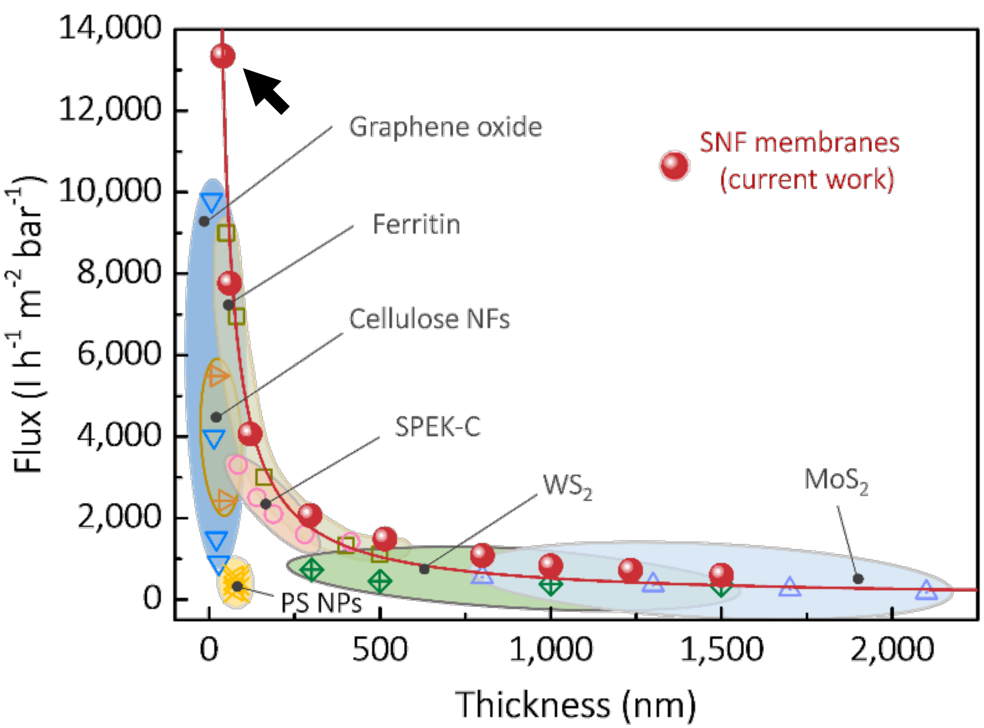
Ling, Jin, Kaplan, Buehler *et al., Nano Letters*, 2016

a



Schematic; rejection of large molecules while allowing small molecules to pass through

b

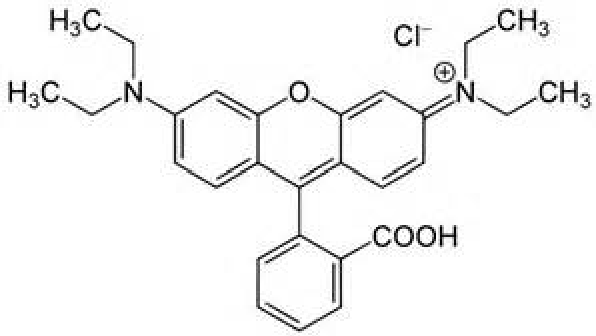


Trends towards high flux compared to other thicknesses

Flux of 40-nm-thick SNF membrane up to 13,000 l h^{-1} m^{-2} bar^{-1}, more than 1,000 times higher than commercial ones

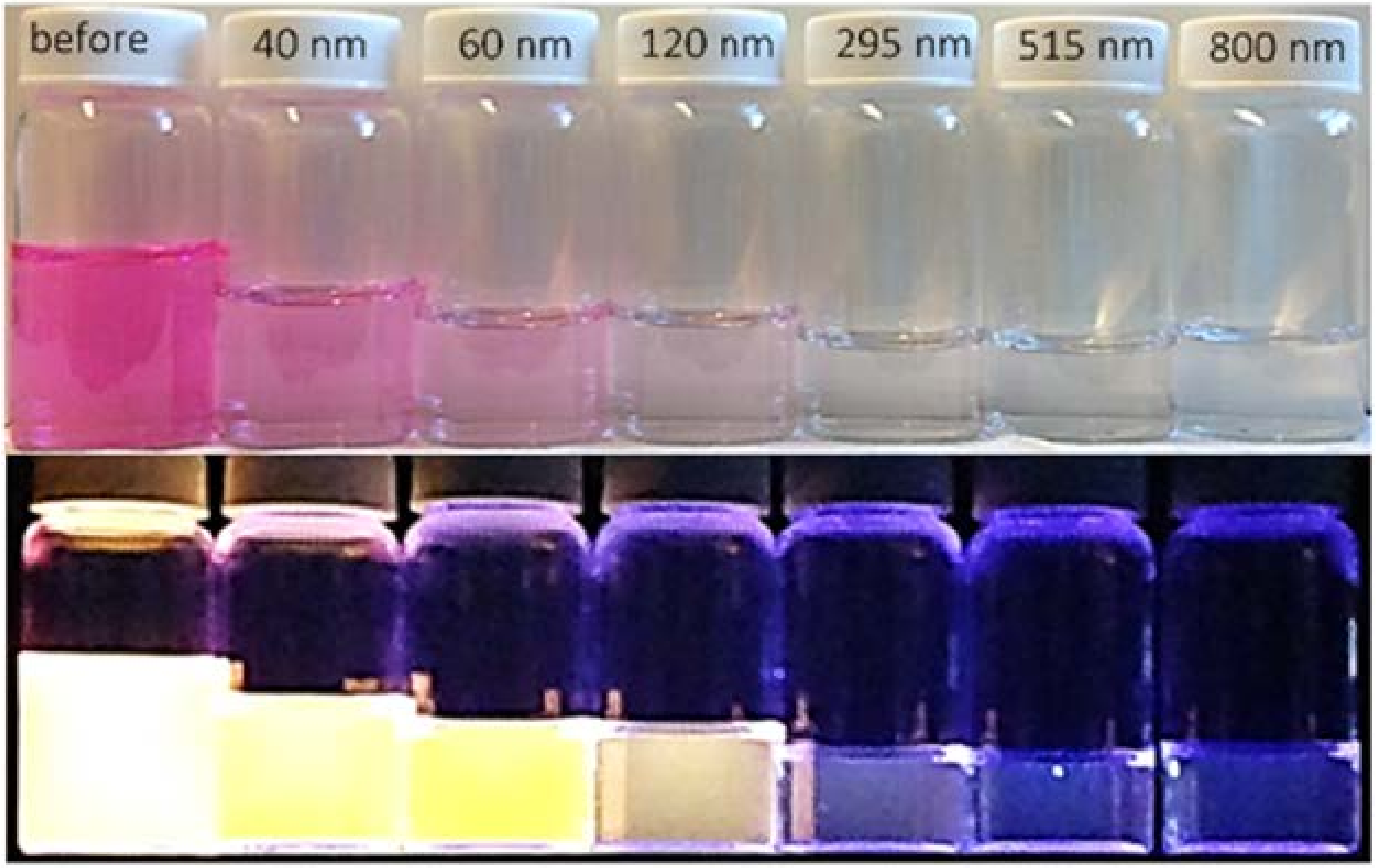
Test with Rhodamine B

- Chemical compound and a dye
- Often used as a tracer dye within water to determine the rate and direction of flow and transport, fluorescent



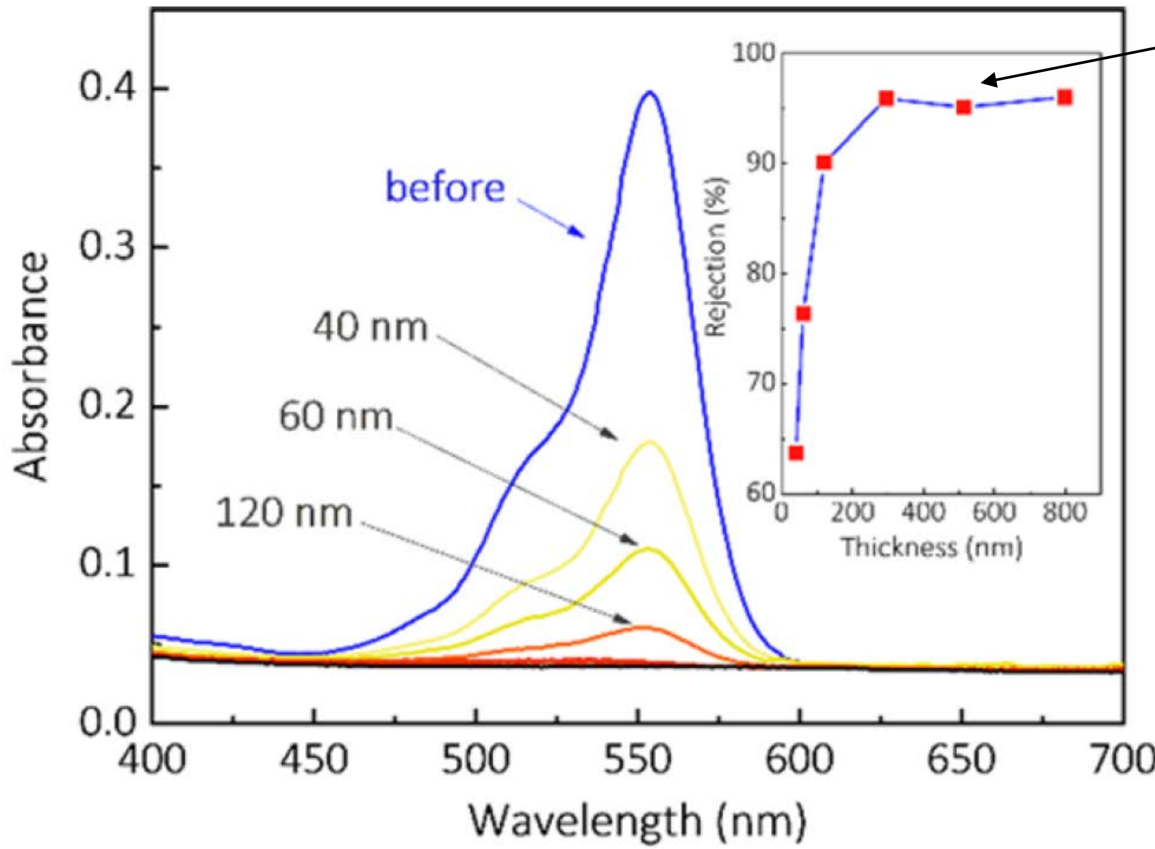
Ling, Jin, Kaplan, Buehler *et al., Nano Letters*, 2016

Before and after filtering Rhodamine B aqueous solutions using SNF membranes with different thicknesses



UV

UV−vis absorption change

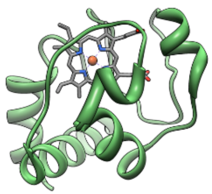


rejection of Rhodamine B aqueous solution with different thicknesses of the SNF membranes

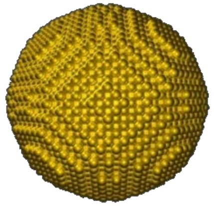
Ling, Jin, Kaplan, Buehler *et al.*, *Nano Letters*, 2016

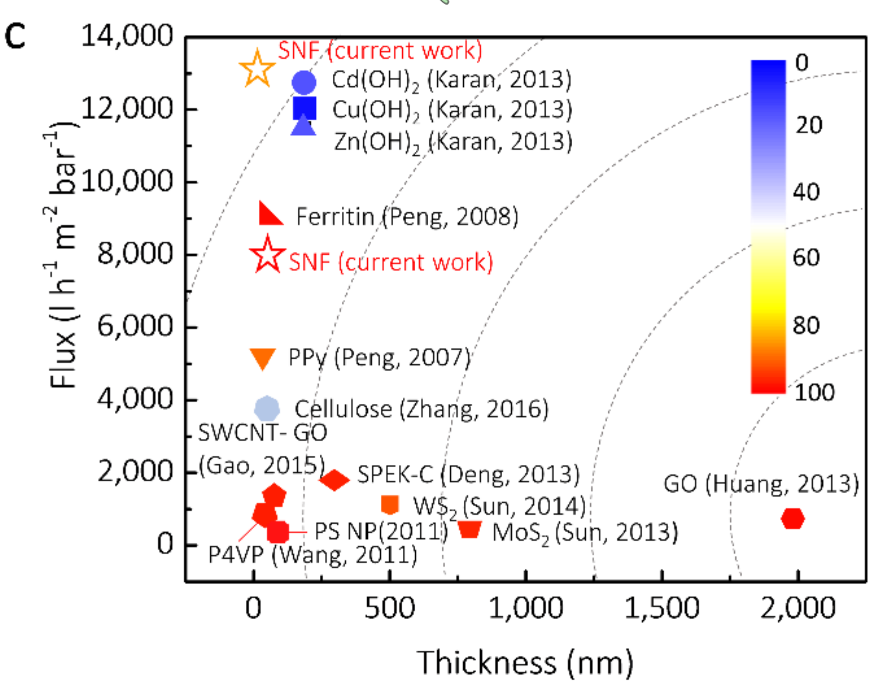
Other examples - separation performance of SNF membranes

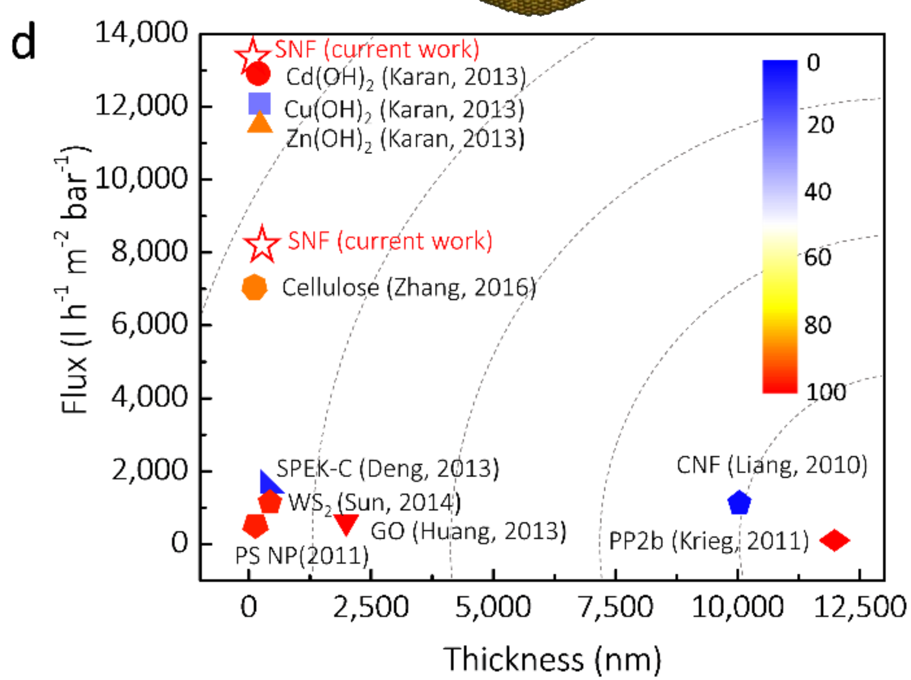
cytochrome c



5 nm gold nanoparticle dispersion





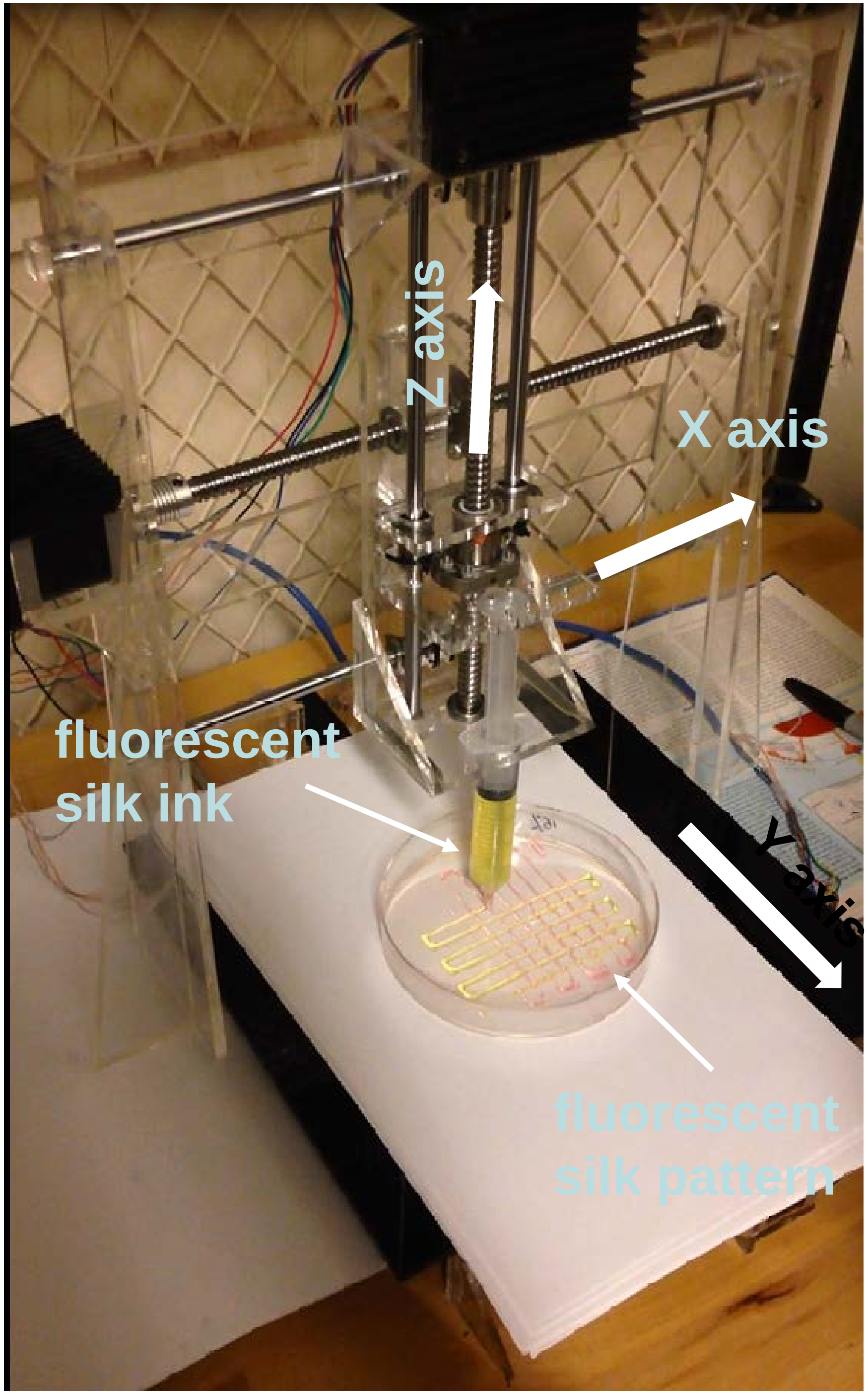


Achieves high flux at high rejection rate with thin membranes

Printing of stretchable silk membranes for **strain measurements**

Ling, Kaplan, Omenetto, Buehler, *et al., Lab On A Chip*, 2016

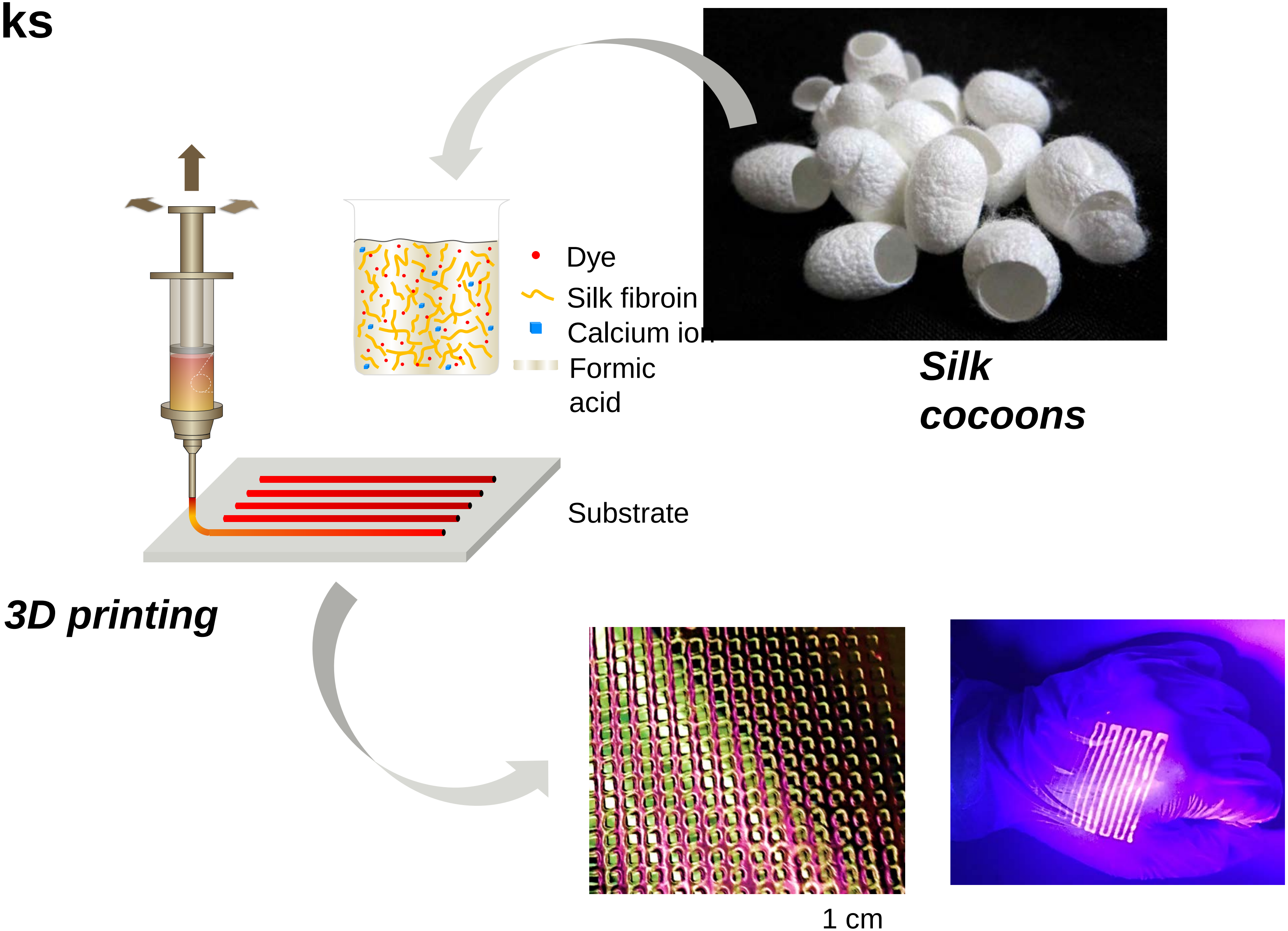
Custom-built printing device

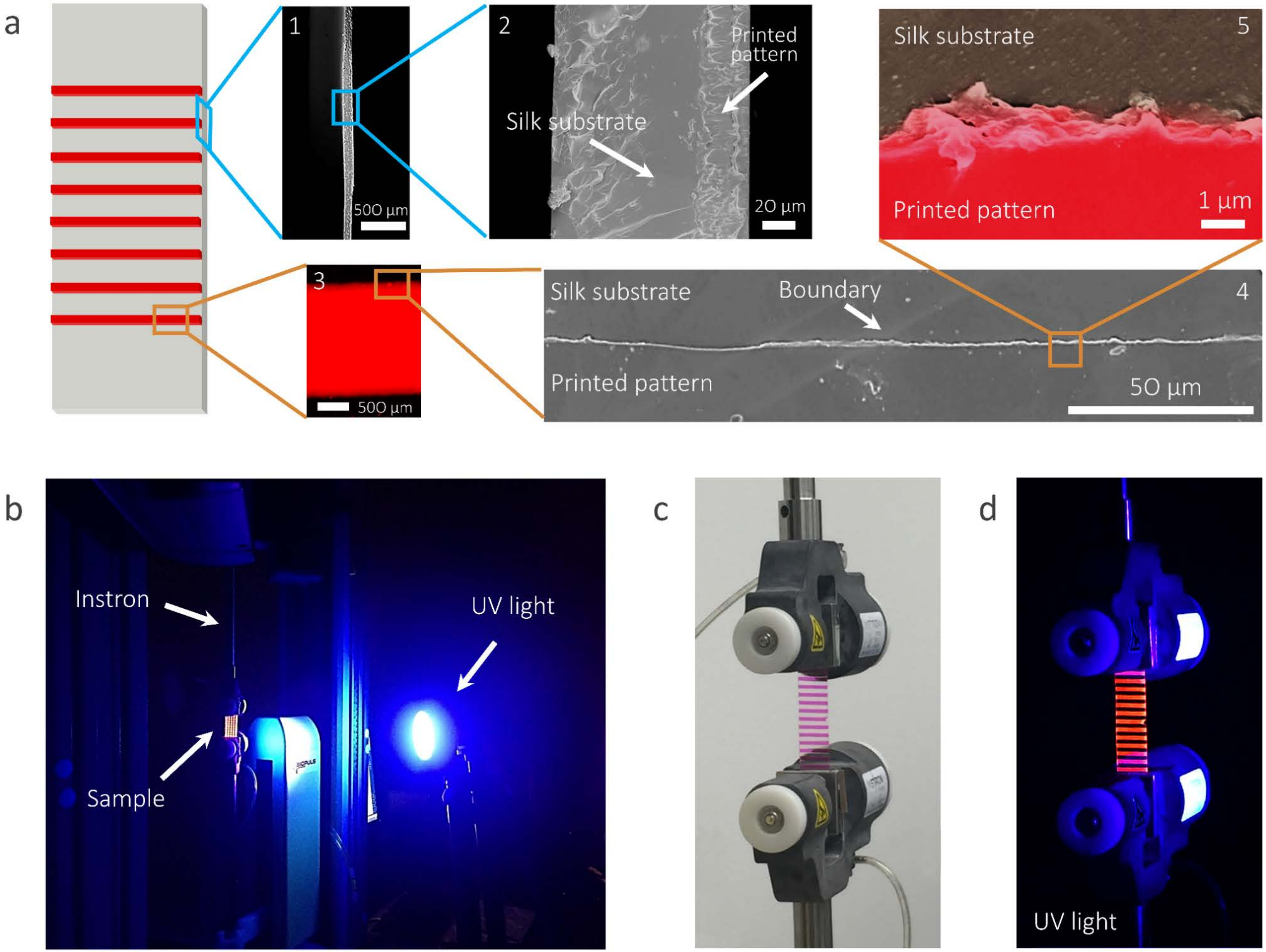


3D printed strain gauges from silk

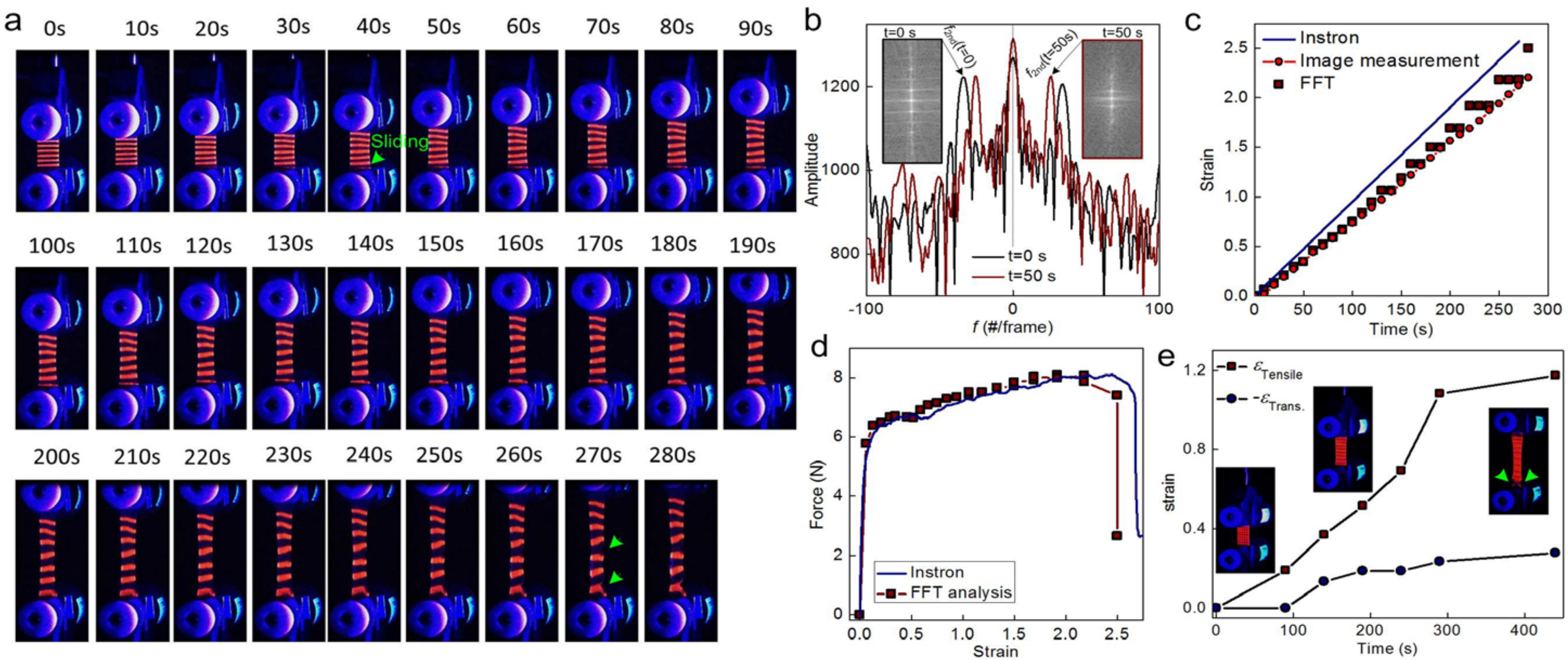
- Quantifying the deformation of biological tissues under mechanical loading is crucial to understand its biomechanical.
- However, strain measurements for biological tissues subjected to large deformations/humid environments are difficult -- due to several limitations such as strain range, boundary conditions, surface bonding and biocompatibility.
- Here we use of silk 3D printing to synthesize strain gauges for large strain measurements in biological tissues.
- Silk-based strain gauges can be stretched up to 1300% without failure, which is more than two orders of magnitude larger than conventional strain gauges, and the mechanics can be tuned by adjusting ion content.
- The printing approach can accurately provide well bonded florescent features on the silk membranes using designs which can accurately measure strain in the membrane. New strain gauges measure large deformations in the materials by eliminating effects of sliding from the boundaries, making measurements more accurate than direct outputs from tensile machines.

3D printing of fluorescent silk inks

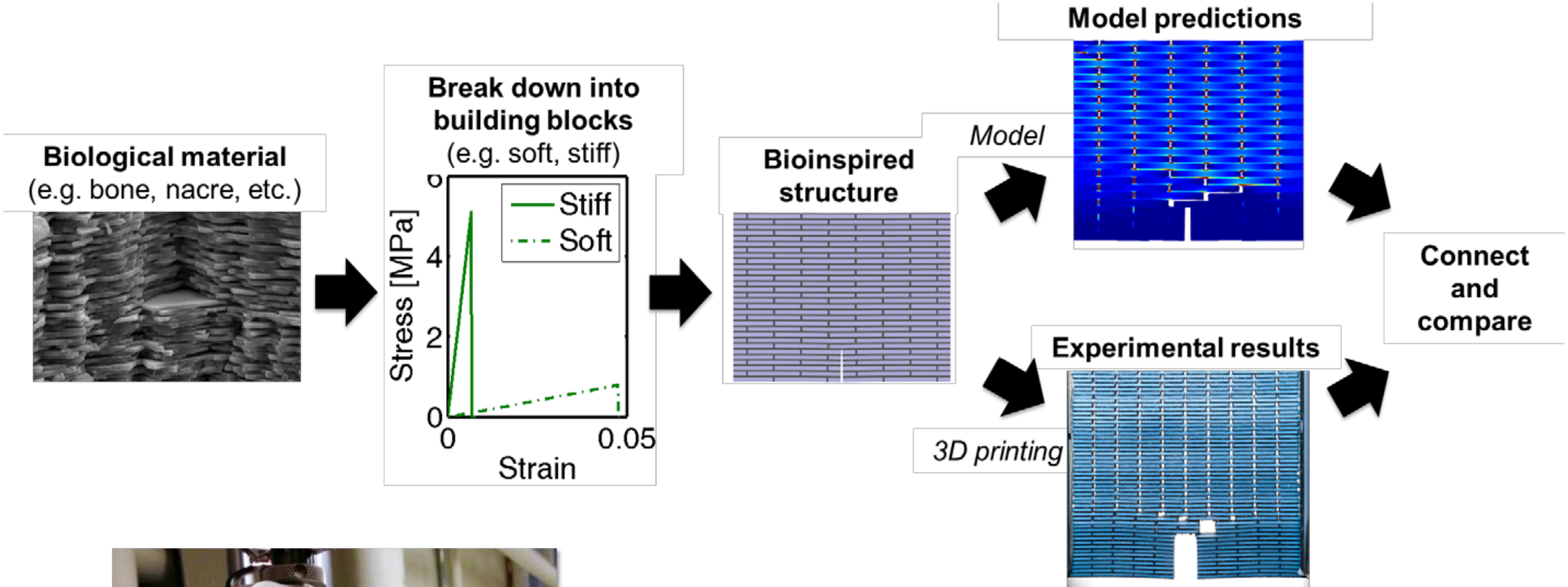


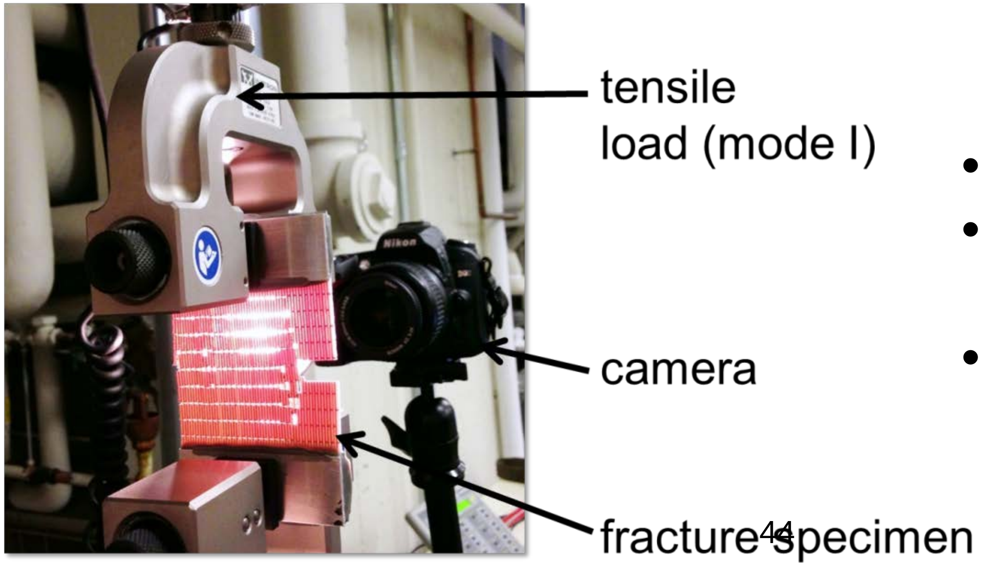


a
1
500 µm
2
Printed pattern
Silk substrate
20 µm
5
Silk substrate
Printed pattern
1 µm
3
500 µm
Silk substrate
Boundary
4
Printed pattern
50 µm
b
Instron
UV light
Sample
c
d
UV light


a
0s
10s
20s
30s
40s
50s
60s
70s
80s
90s
Sliding
100s
110s
120s
130s
140s
150s
160s
170s
180s
190s
200s
210s
220s
230s
240s
250s
260s
270s
280s
b
t=0 s
t=50 s
Amplitude
f (#/frame)
t=0 s
t=50 s
c
Instron
Image measurement
FFT
Strain
Time (s)
d
Force (N)
Strain
Instron
FFT analysis
e
strain
Time (s)

From optimization to manufacturing



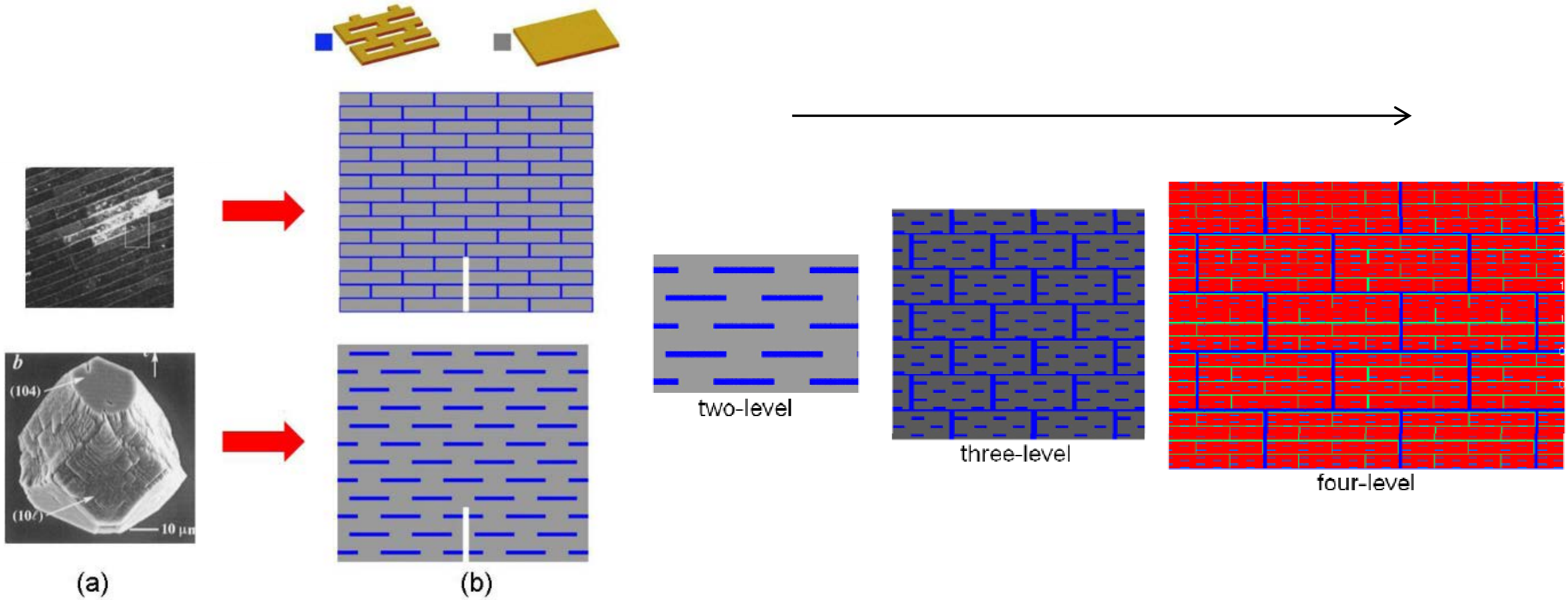


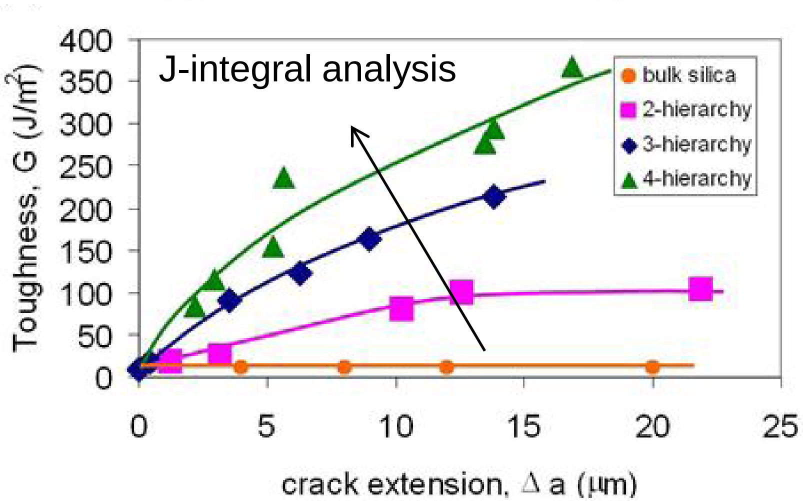
- Samples tested in tension
- Measure force-displacement
- Image deformation/failure mechanisms

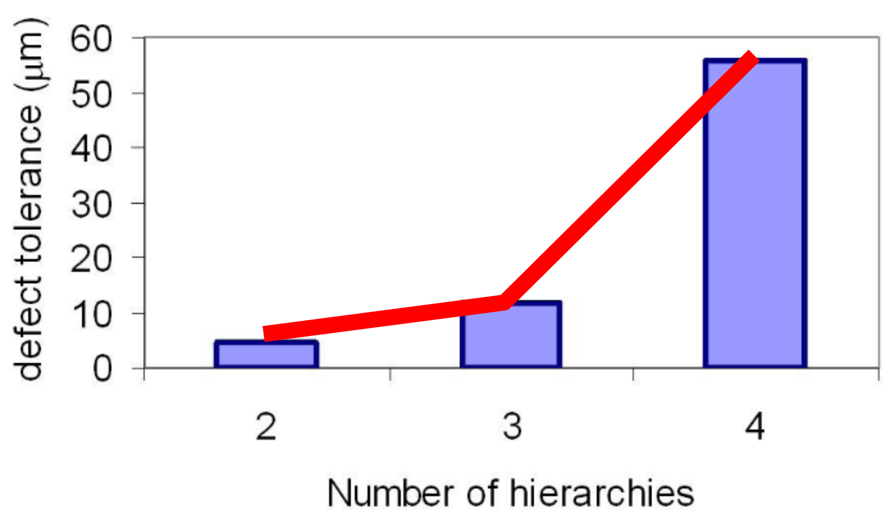
L. Dimas & M. Buehler

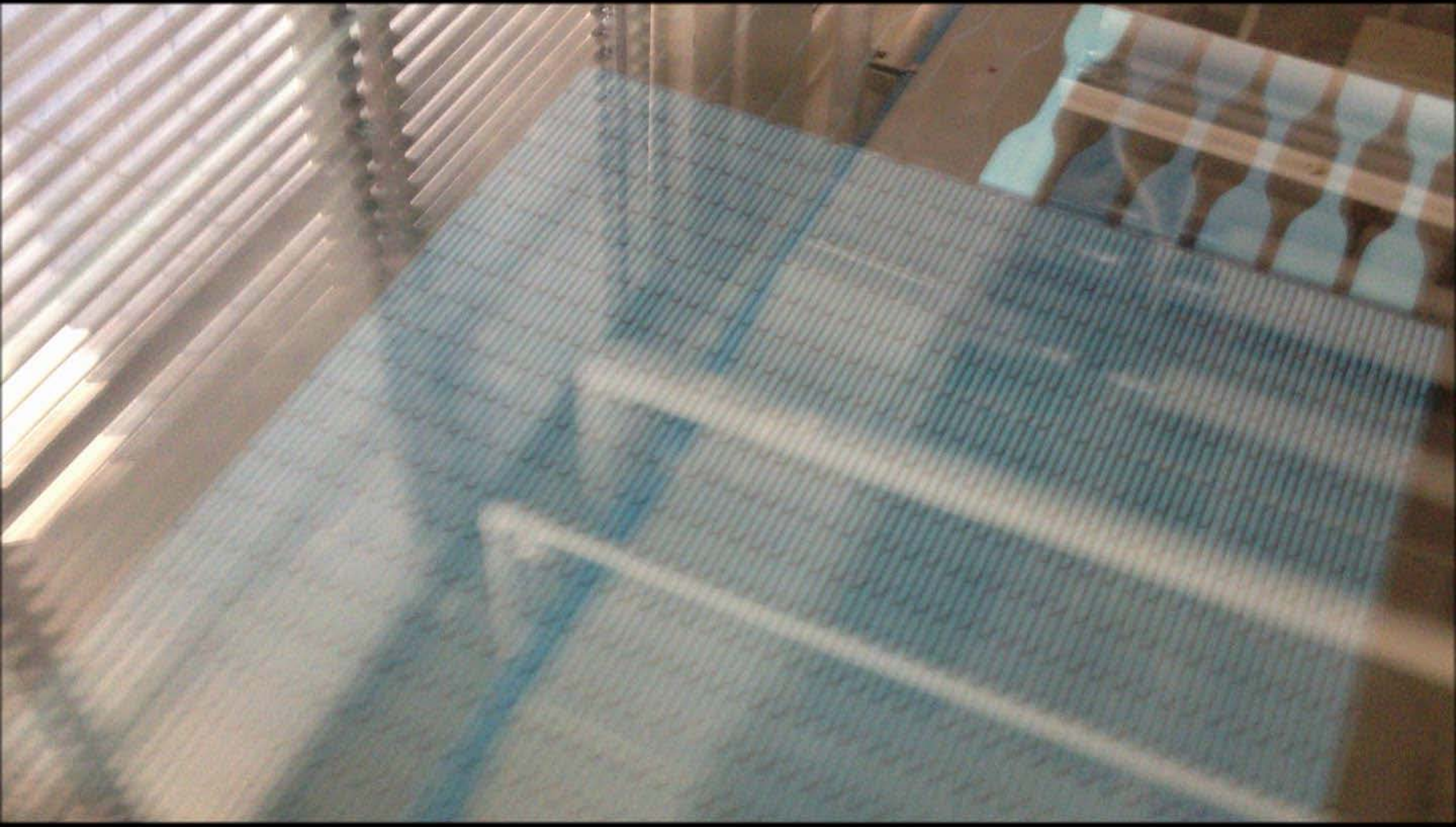
Hierarchical composites with large toughness

Sen, Buehler, *Scientific Reports*, 2011

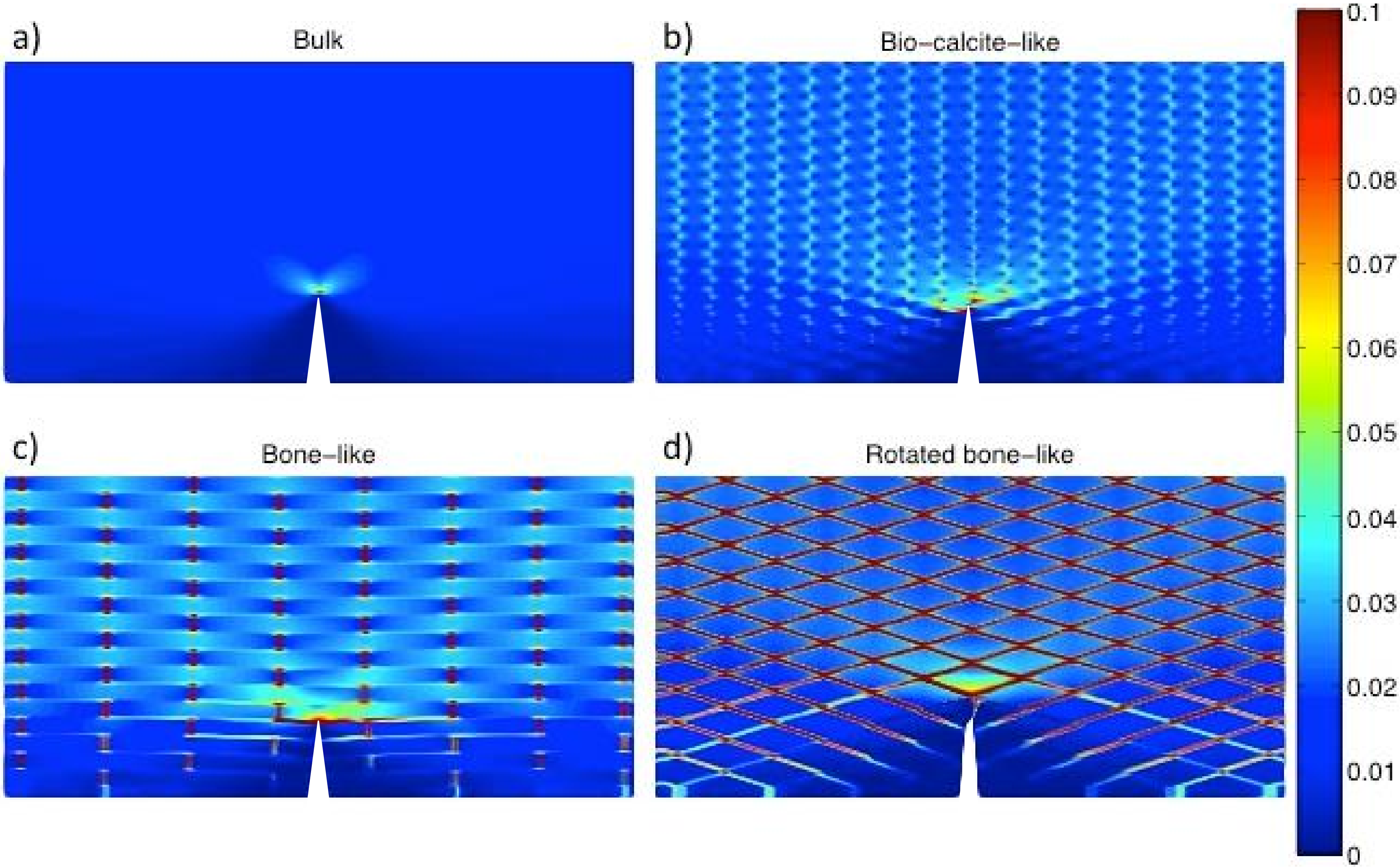








Bioinspired designs



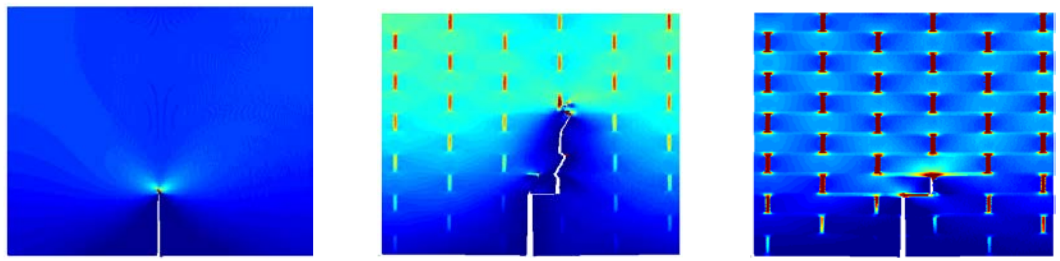
L. Dimas *et al.*, 2012

Tuning Interactions with Constitutive Laws

Longitudinal Strain-fields

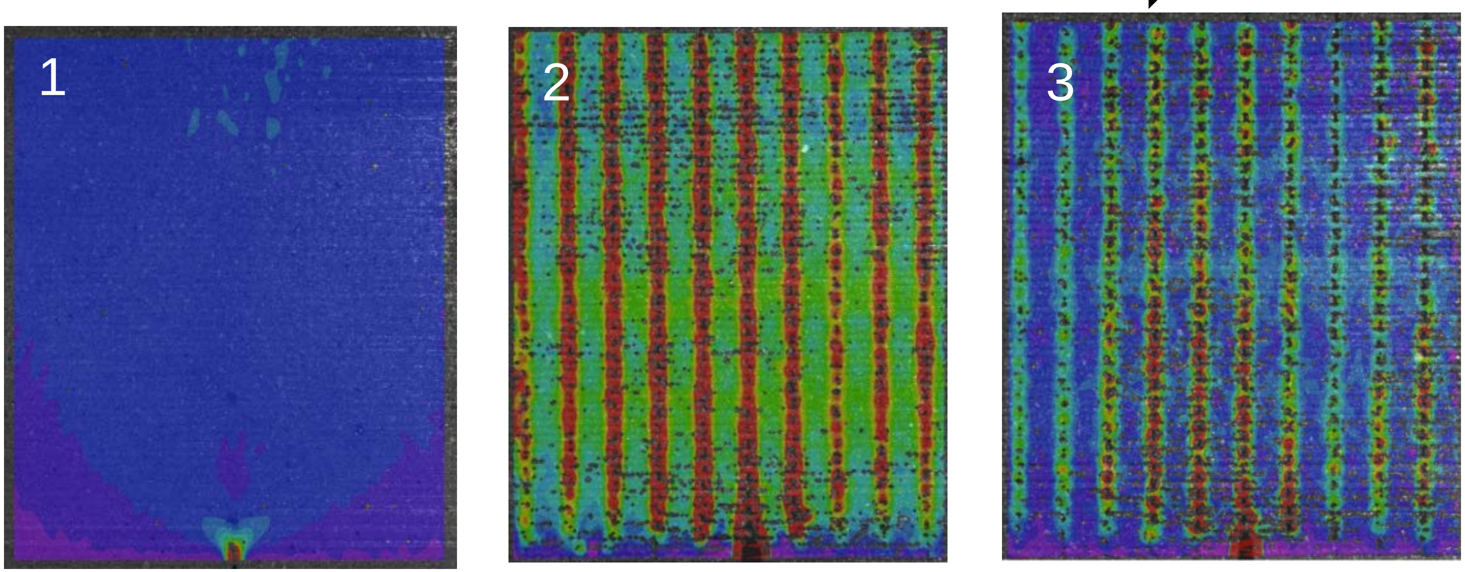
As matrix becomes more compliant deformation mechanisms change – delocalized loading at the cost of stiffness loss – optimum in the middle

Simulation



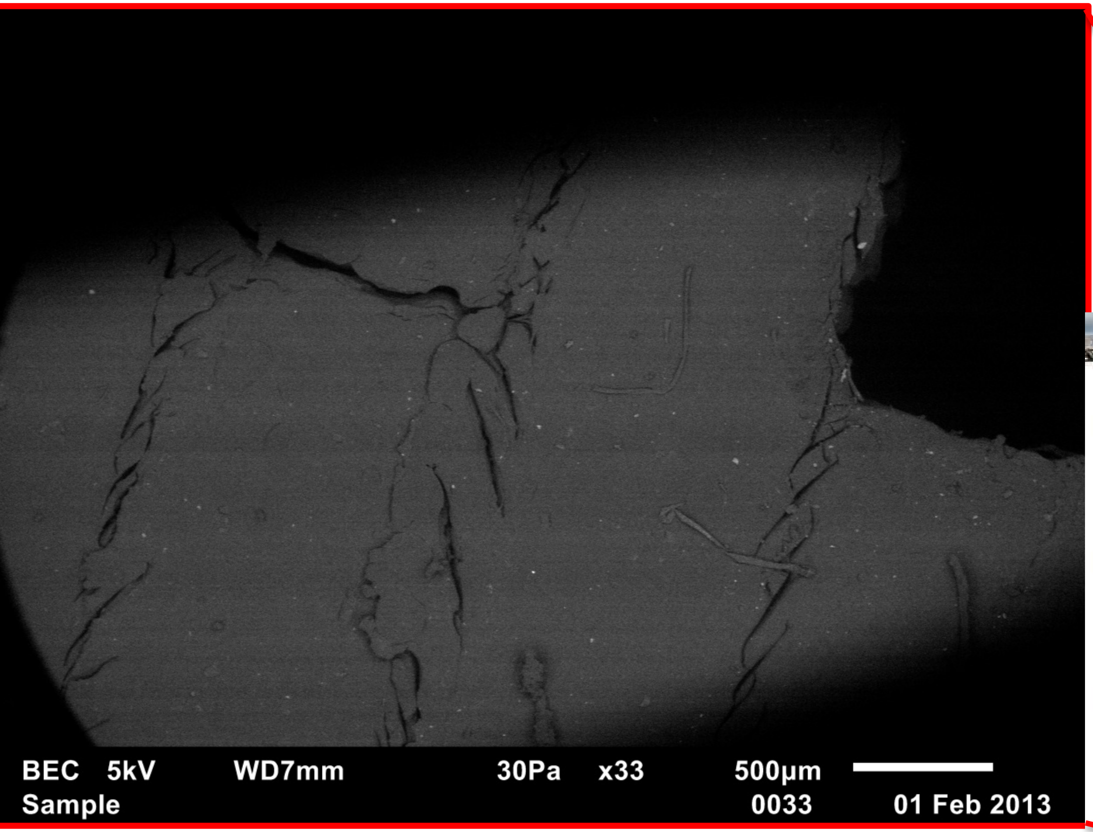
Increasing compliance of matrix phase

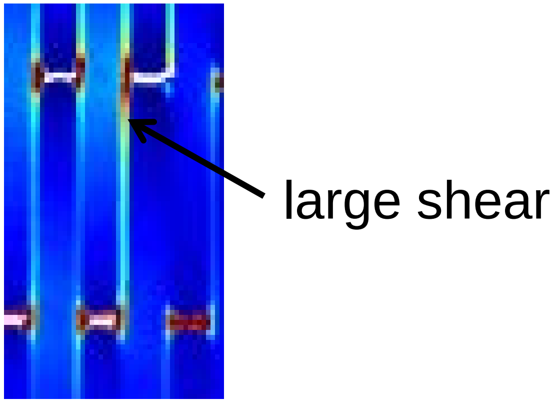
Experiment

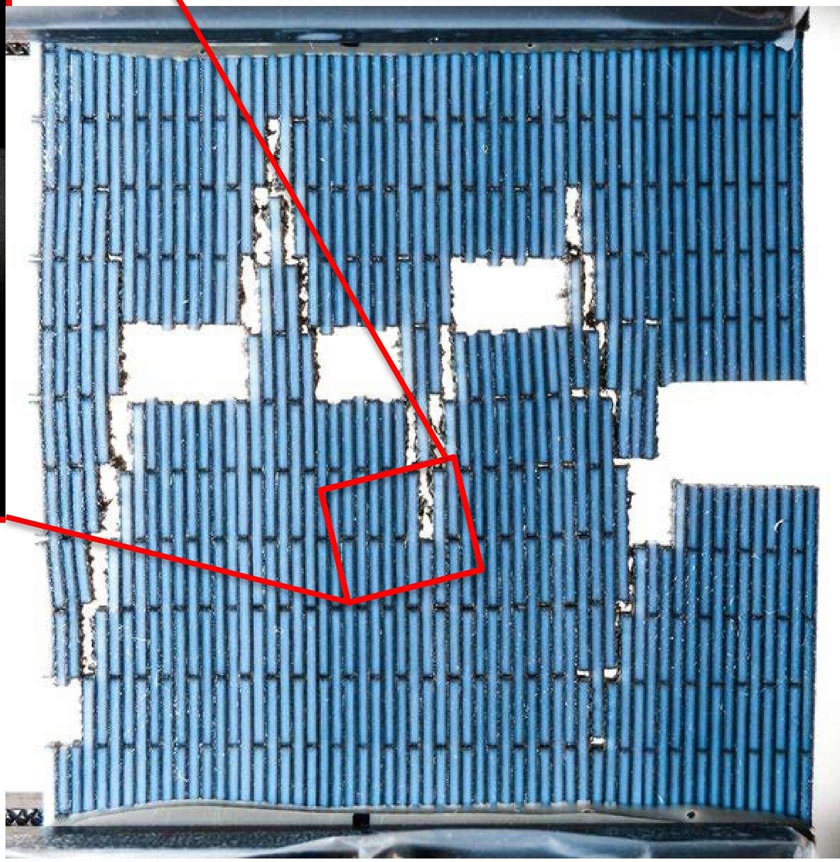


L. Dimas & M. Buehler, Soft Matter, 2015

SEM analysis of failure mode

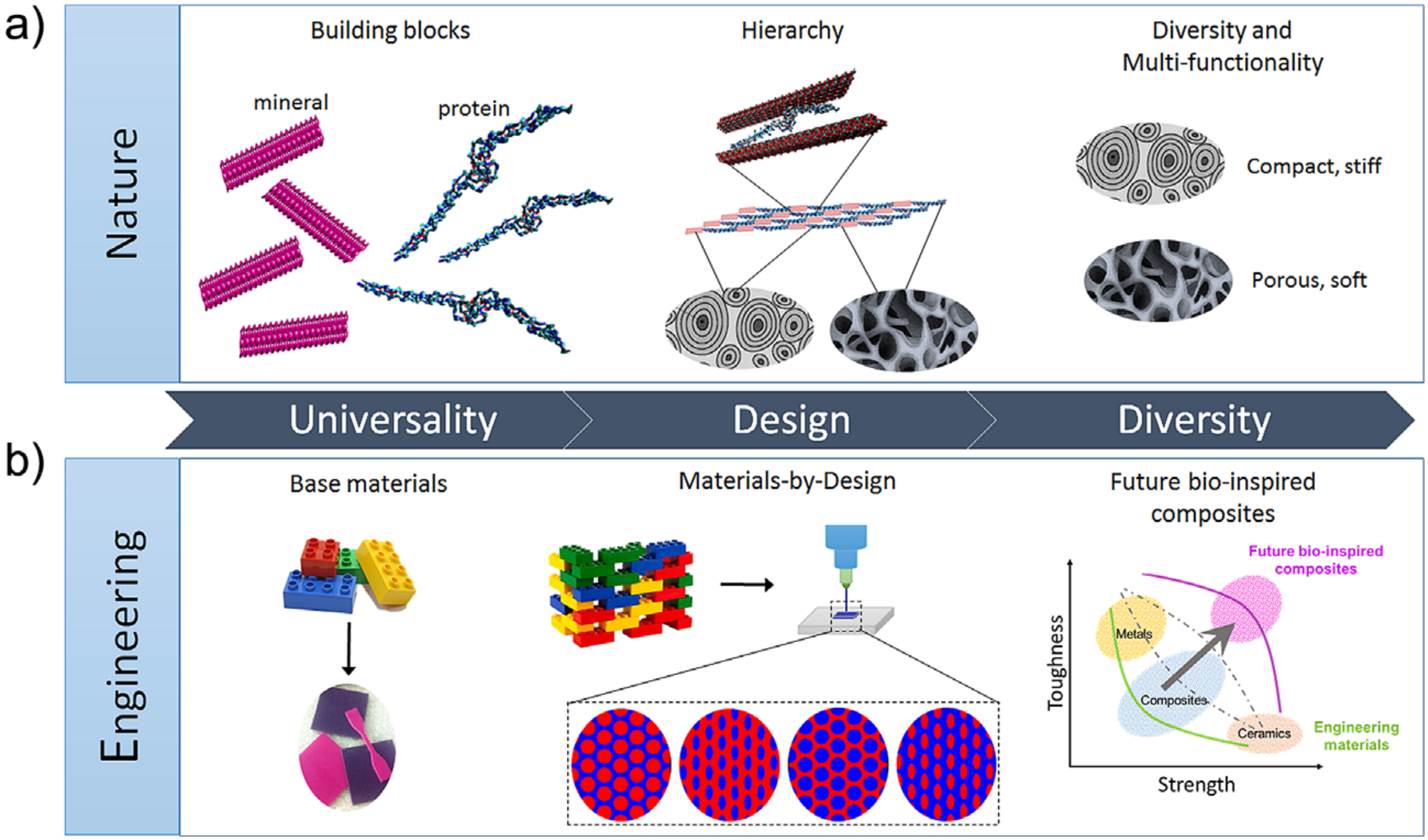




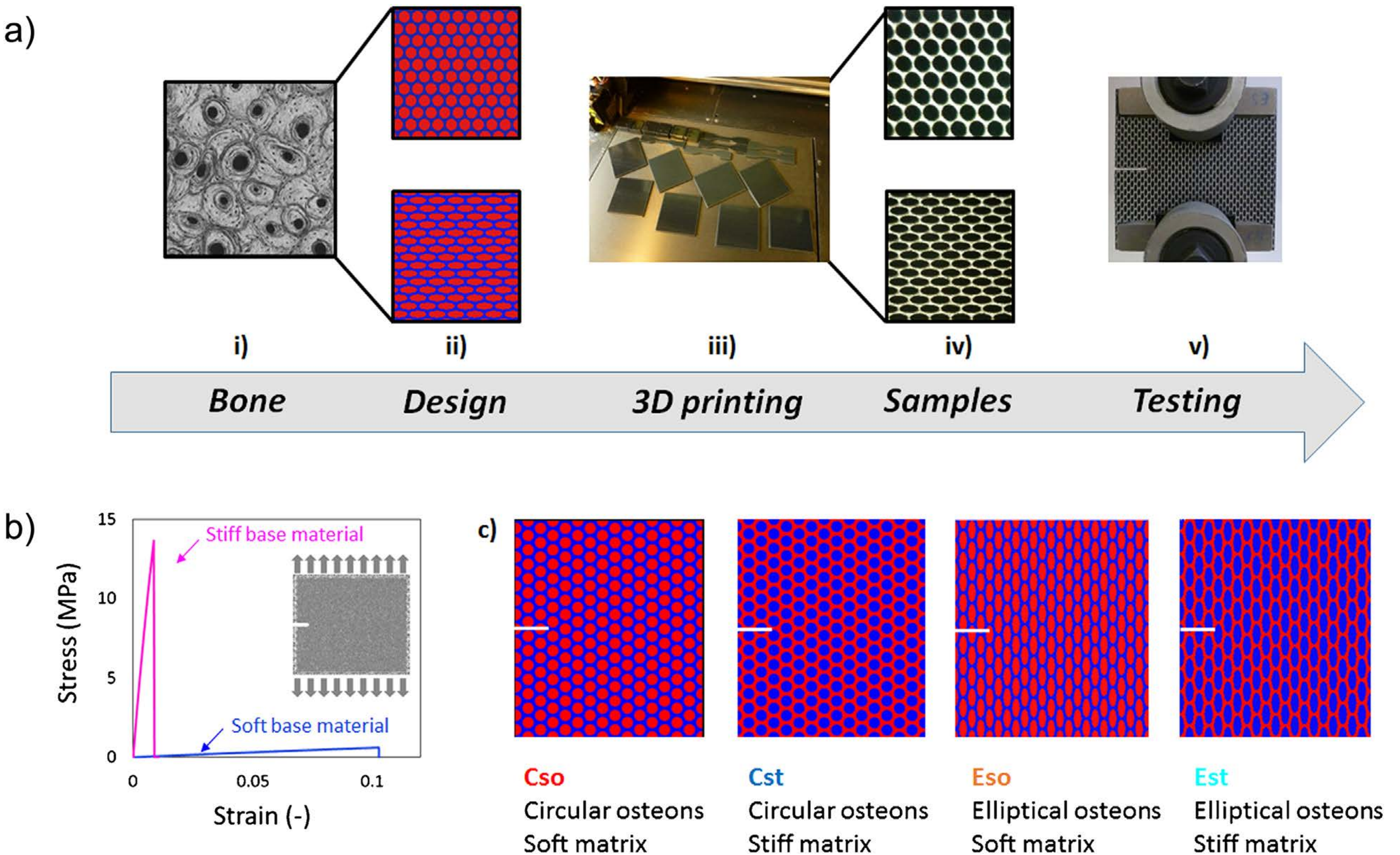


Distributed Failure

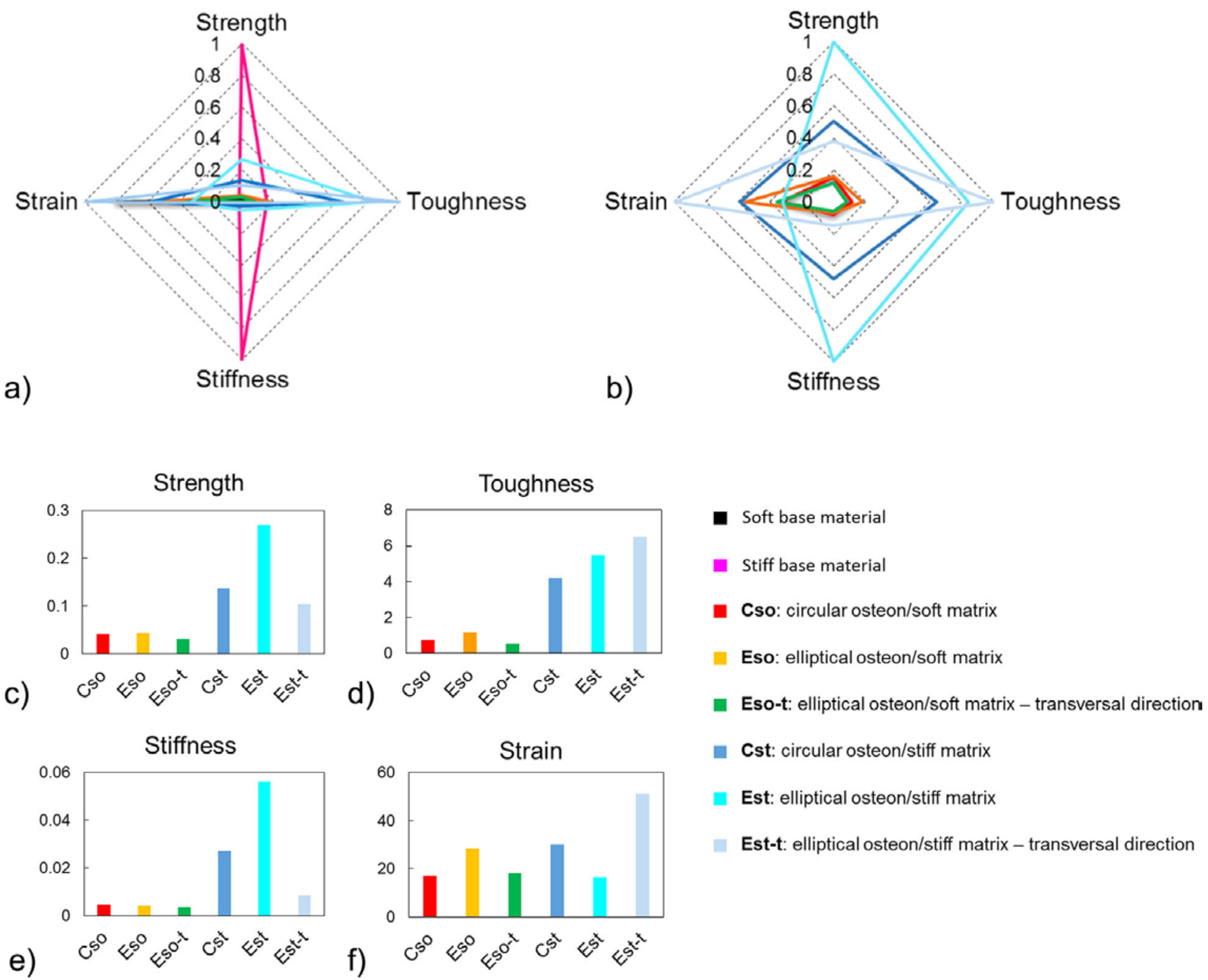
Universality-diversity paradigm



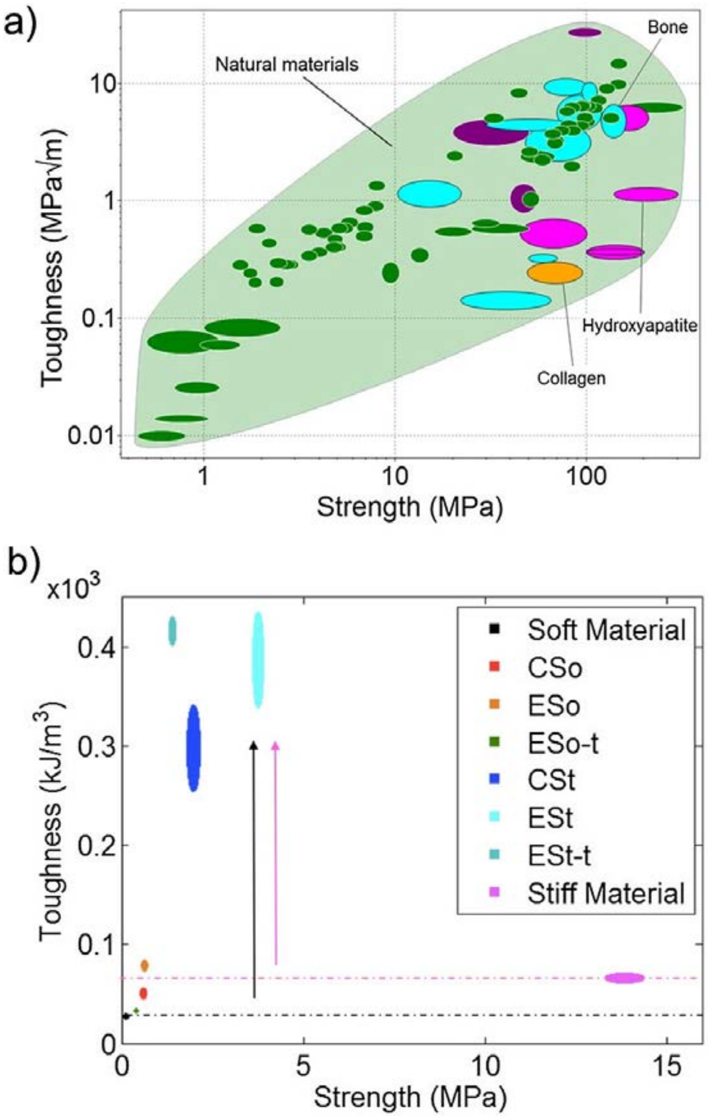
Bone-inspired composites



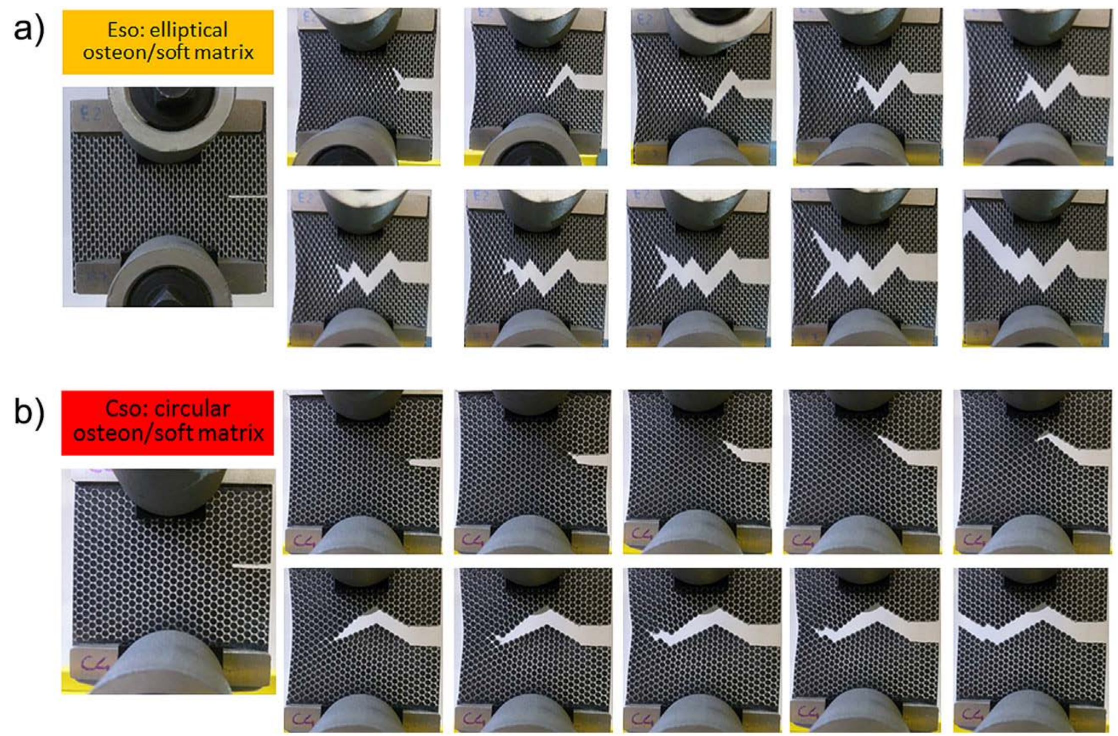
Effect of designs on key mechanical behavior



Ashby plots

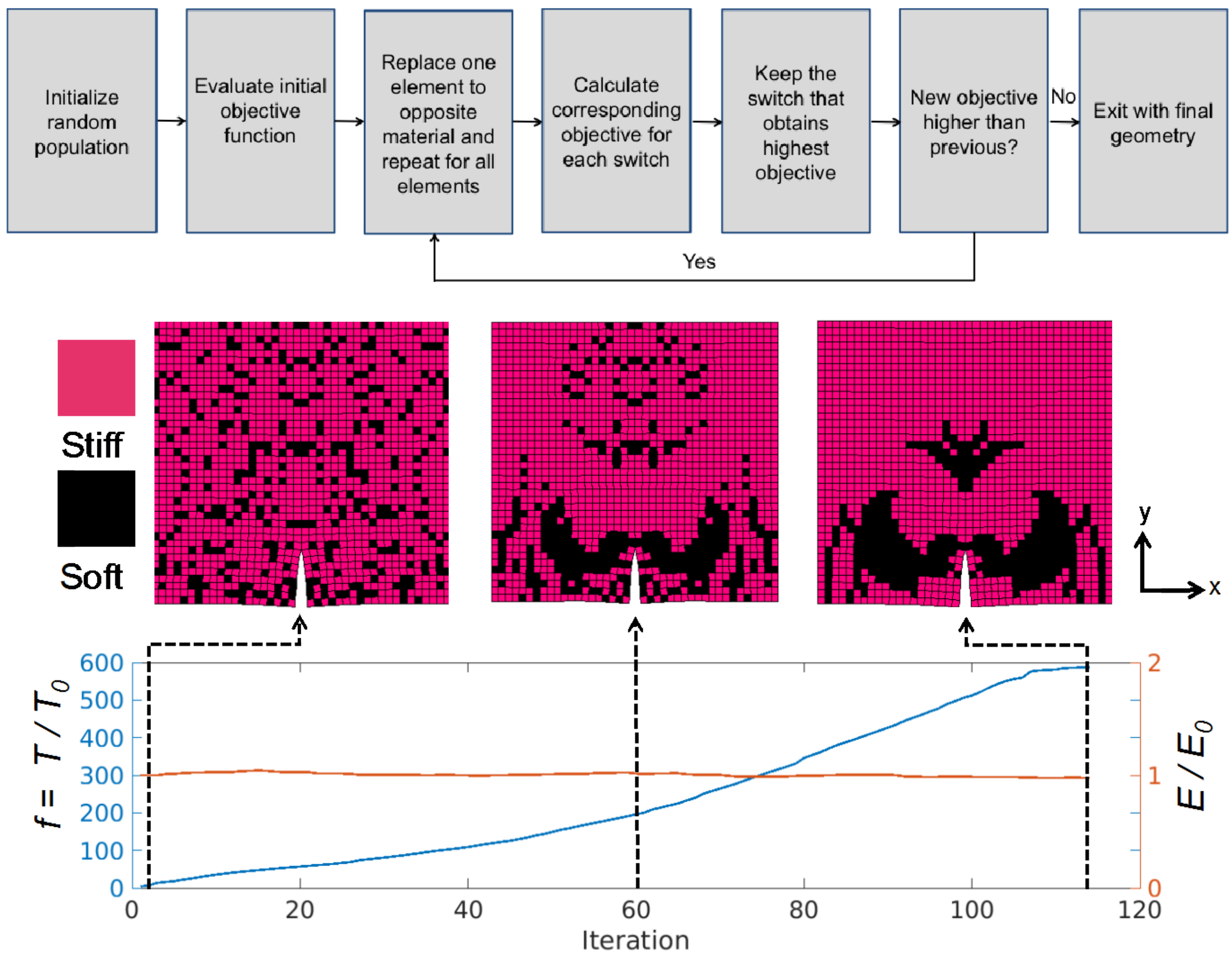


a)
Natural materials
Bone
Hydroxyapatite
Collagen
Toughness (MPa√m)
10
1
0.1
0.01
1
10
100
Strength (MPa)
b)
x10^3
Soft Material
CSo
ESo
ESo-t
CSt
ESt
ESt-t
Stiff Material
0.4
0.3
0.2
0.1
0
Toughness (kJ/m^3)
0
5
10
15
Strength (MPa)



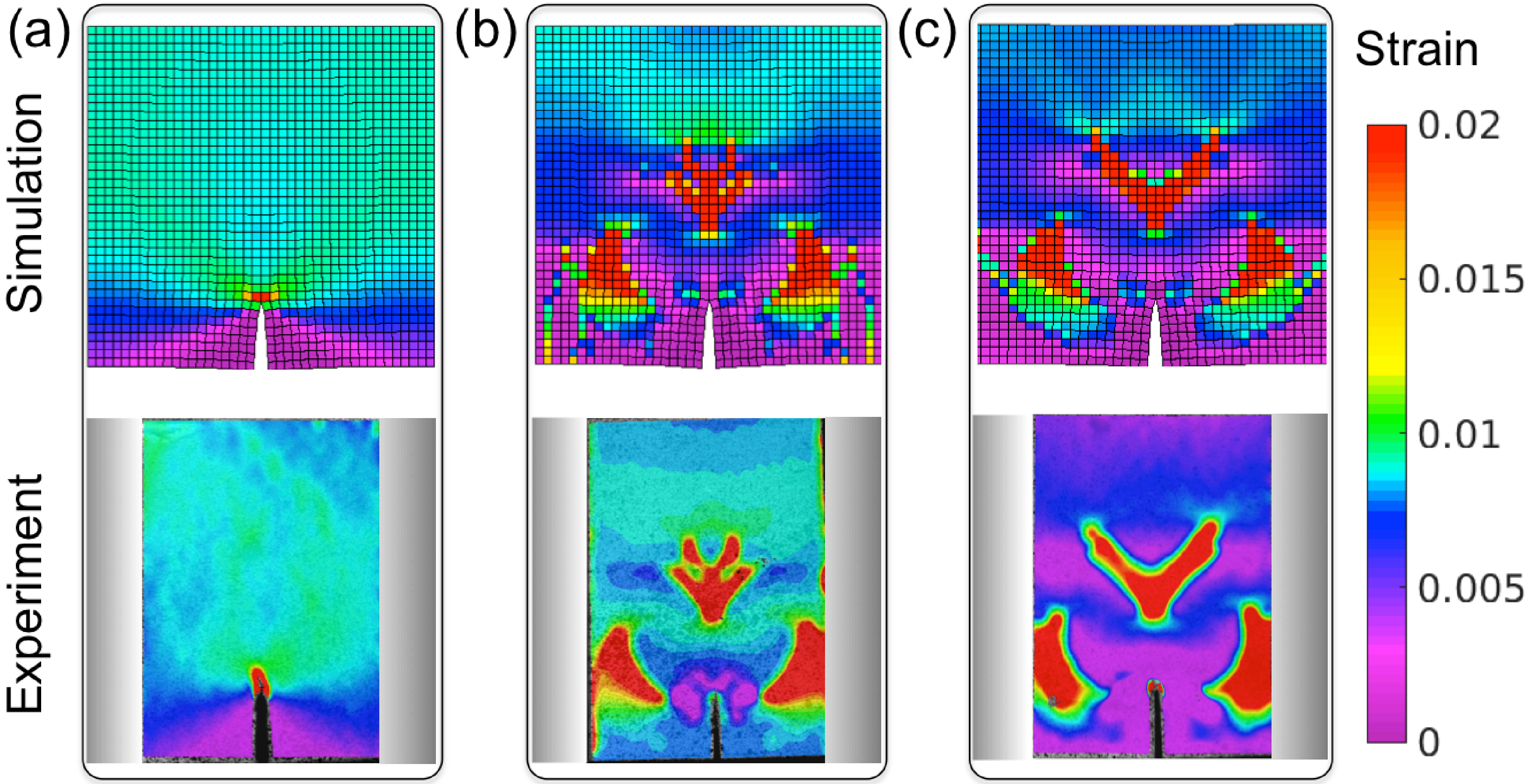
a)
Eso: elliptical osteon/soft matrix
b)
Cso: circular osteon/soft matrix

Find distribution of soft material blocks to optimize the fracture toughness of composites



G. X. Gu, L.,Dimas, Z. Qin, M. J. Buehler et al.,, Journal of Applied Mechanics, 2016
G. X. Gu, S. Wettermark, and M. J. Buehler, in submission

Comparison between simulations and experiments (cont'd)

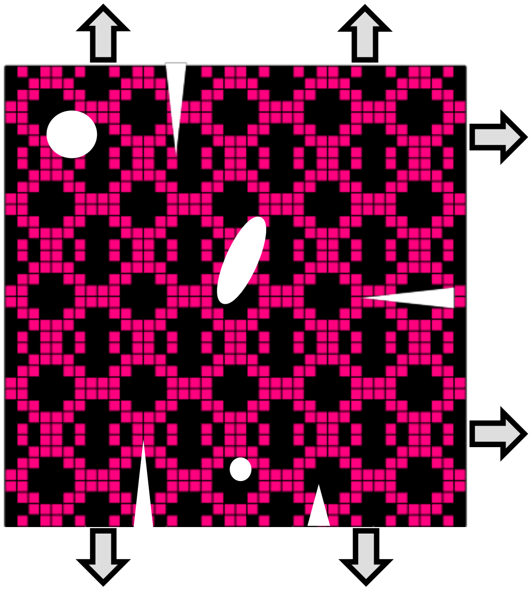


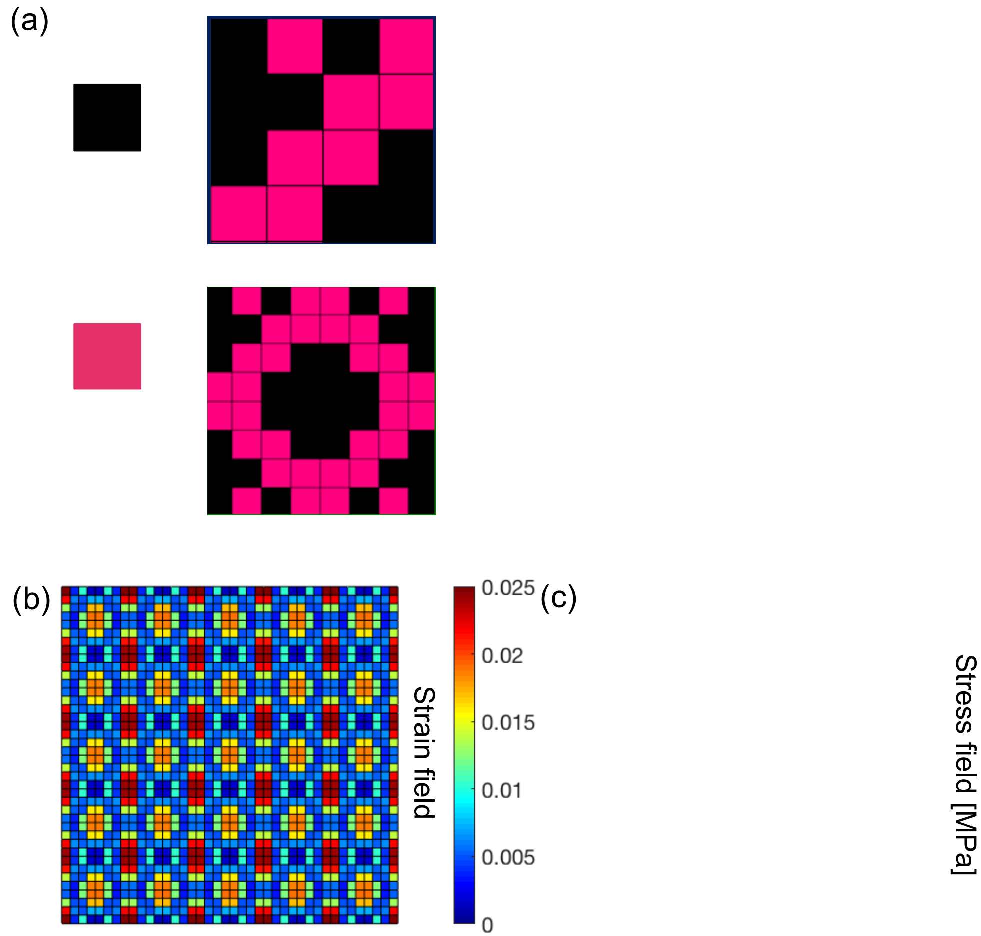
Composite microstructure optimization for fracture resistance

Massachusetts Institute of Technology

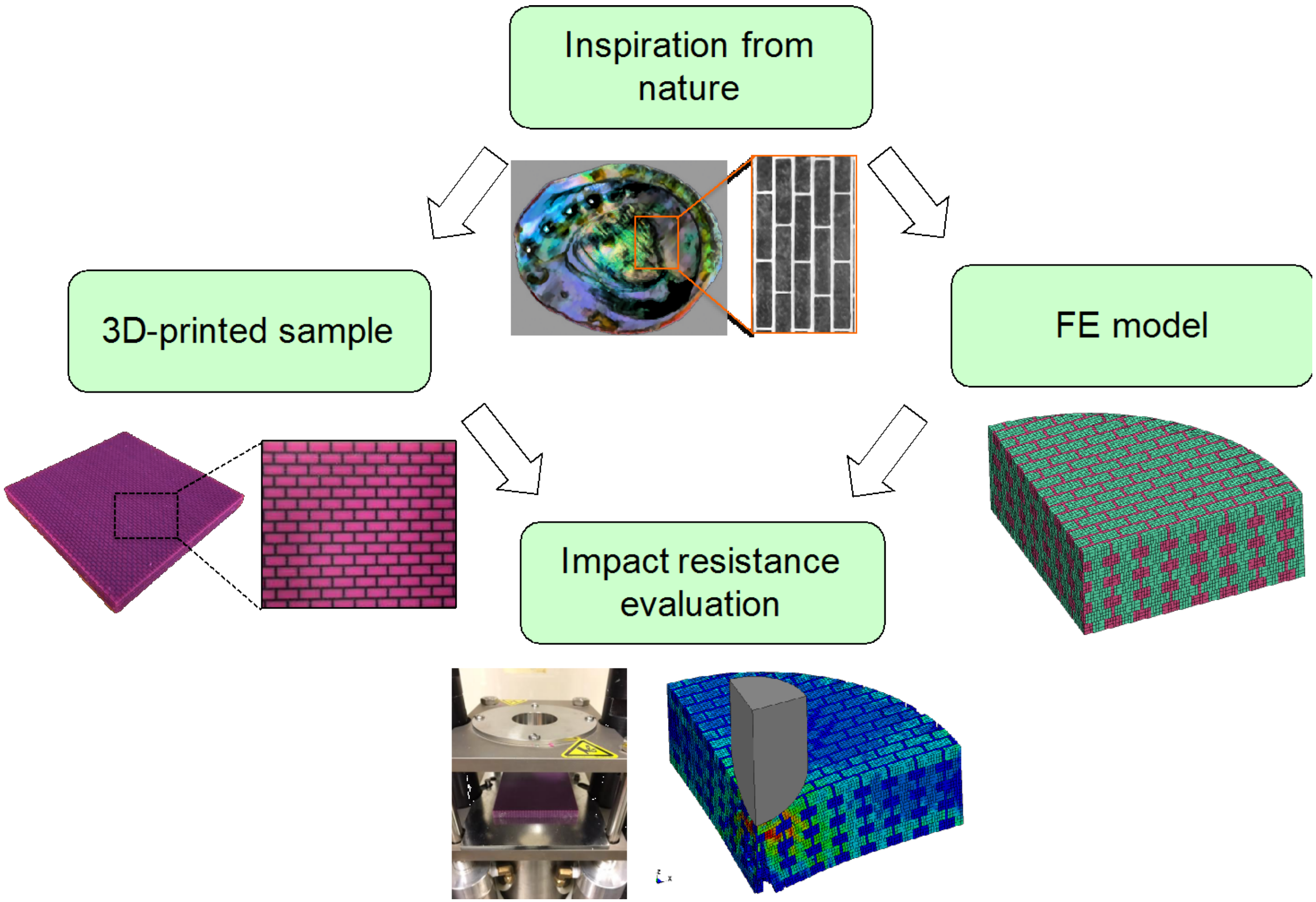
LABORATORY FOR ATOMISTIC & MOLECULAR MECHANICS

Can we optimize composites for arbitrary cracks?

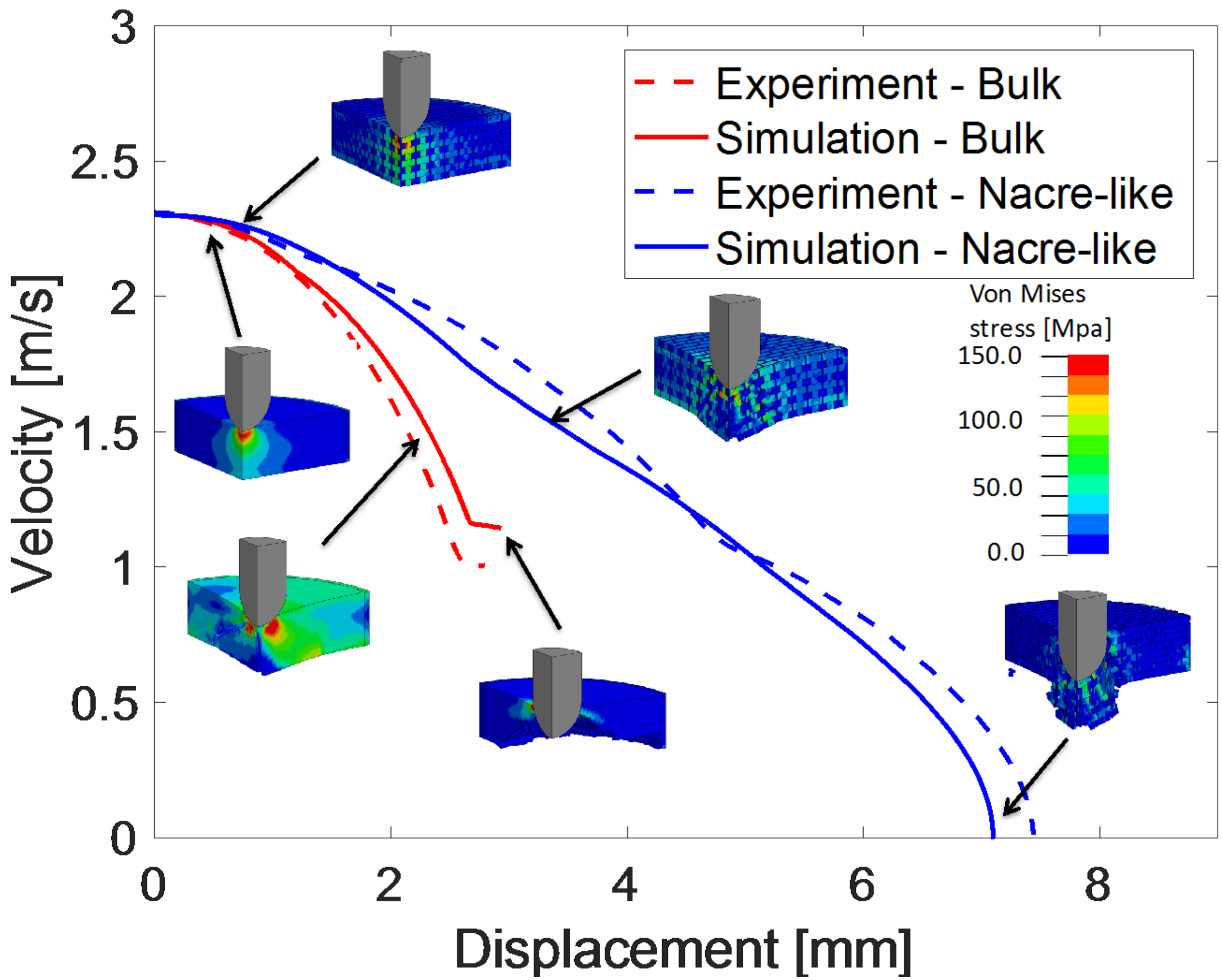


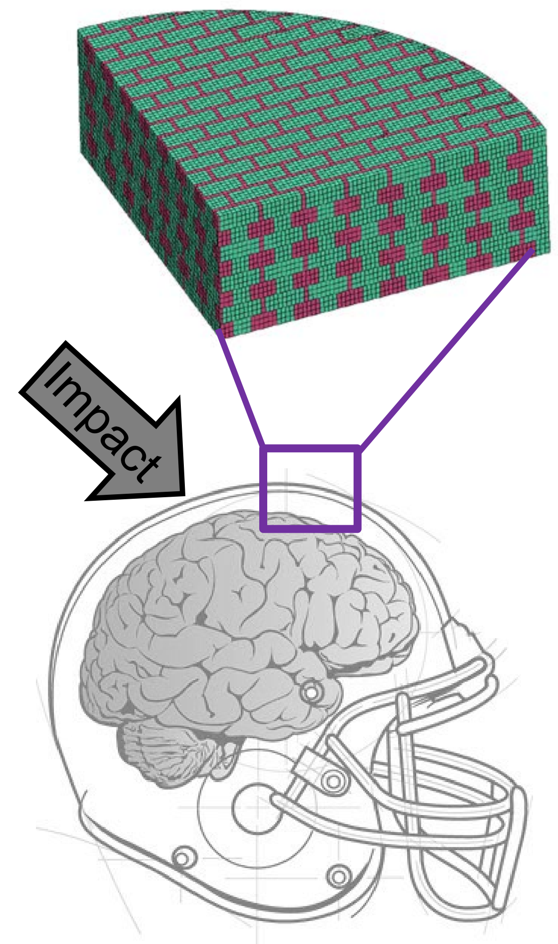


Design of impact resistant smart composites

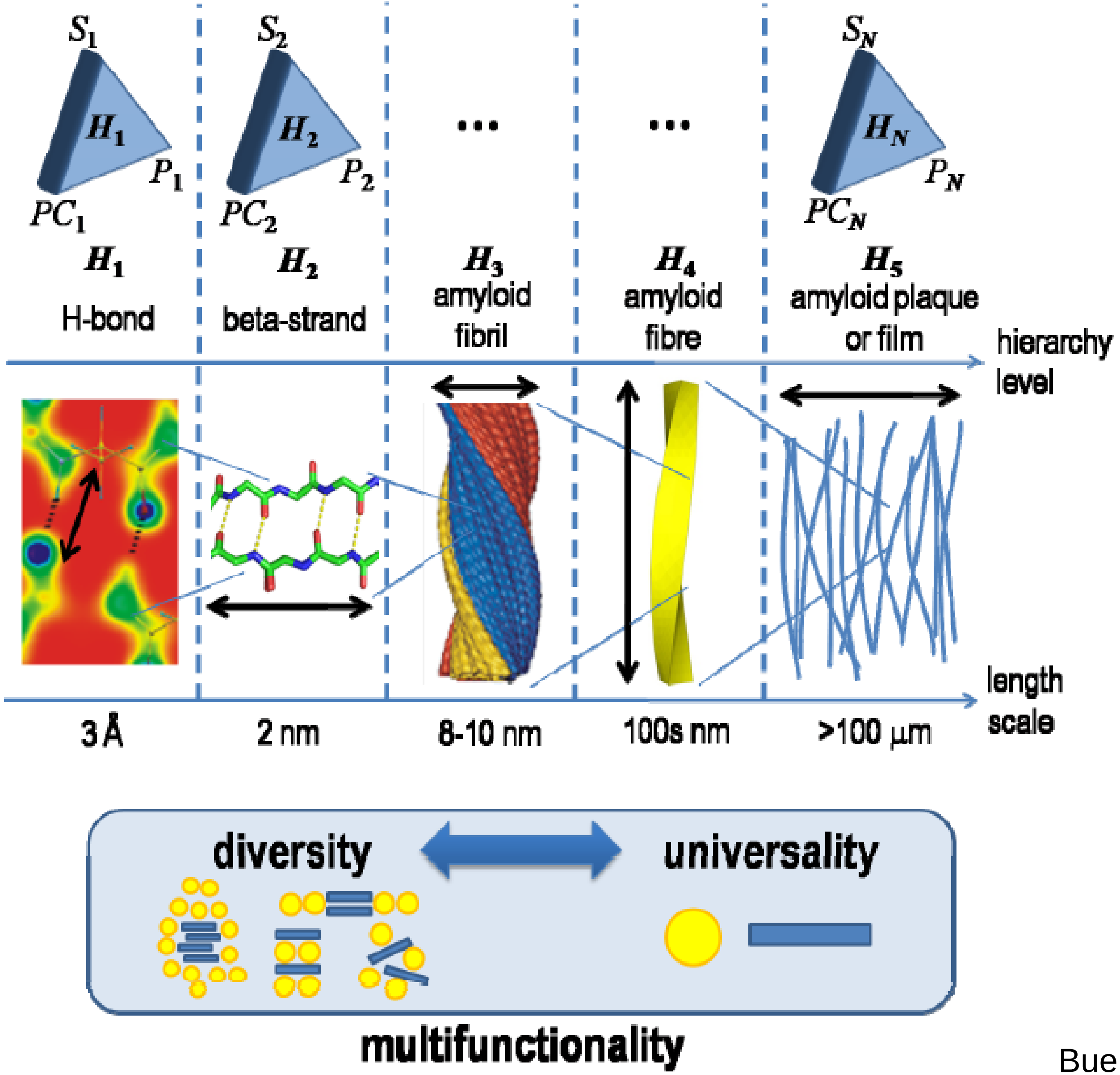


Future protective applications





Universality-diversity paradigm



*Create multifunctionality (**diversity**) by changing structural arrangements of few (**universal**) constituents rather than inventing new building blocks*

Buehler, *Nature Nanotechnology*, 2010

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