

Structural Biopolymers: using Nature's building blocks as an inspiration for advanced manufacturing

Benedetto Marelli, Laboratory for Advanced Biopolymers, CEE @ MIT

Biomaterials tomorrow

- bio-instructive
- respond to their surroundings
- transform themselves
- disappear harmlessly
- biocompatible without sacrificing technological performance
- have "non-obvious" functions



Brief Bio

Benedetto Marelli

Paul M. Cook Career Development Professor
Civil and Environmental Engineering – MIT

B.Eng. – Biomedical Engineering – Politecnico di Milano ('05)

M.Sc. – Biomedical Engineering – Politecnico di Milano ('08)

Ph.D. – Materials Science and Eng. – McGill University ('12)

Postdoc – Biomedical Engineering – Tufts University

Structural biopolymers synthesis, assembly and fabrication

Materials for agriculture, food safety and food security

Materials for regenerative medicine, sensors and optoelectronics

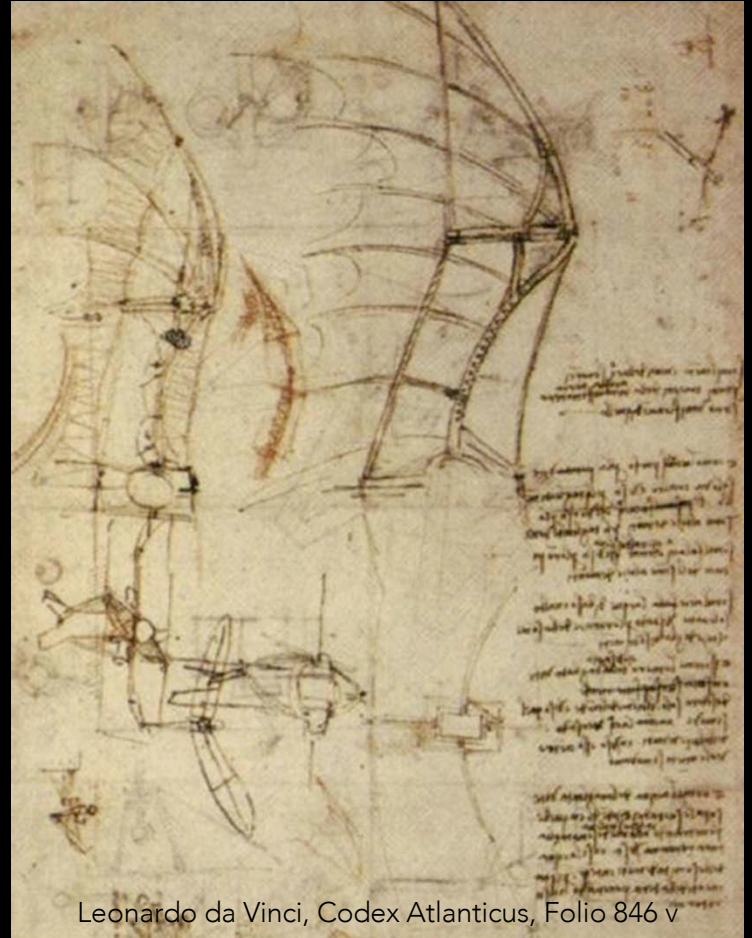
Soil Engineering

Nature as source of inspiration

From mythology...



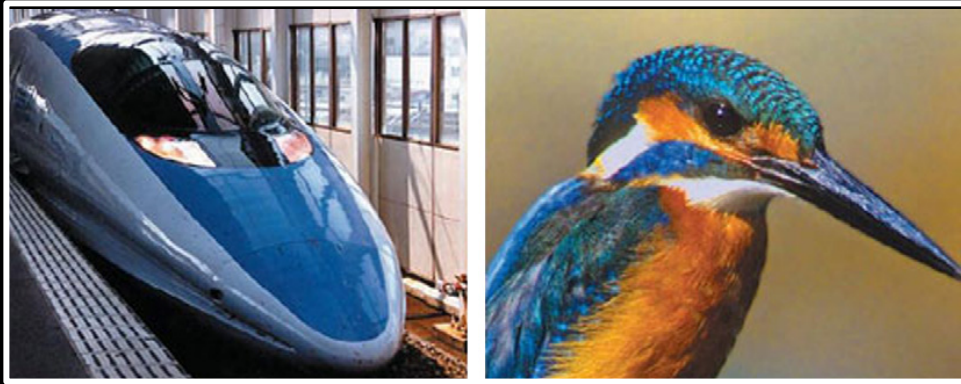
Daedalus and Icarus, Charles Paul Landon



Leonardo da Vinci, Codex Atlanticus, Folio 846 v

...to the study of innovative solutions

Nature as source of inspiration for engineering innovative solutions...



Shinkansen train nose

Kingfisher's beak

Bioinspiration Biomimicry

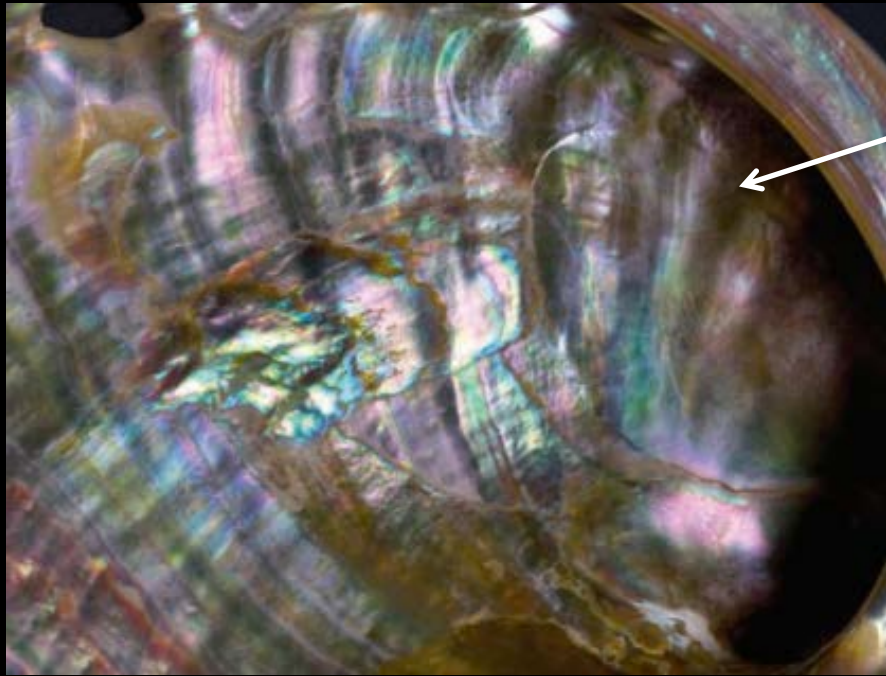


Falcon wing feather



Thermal chimneys

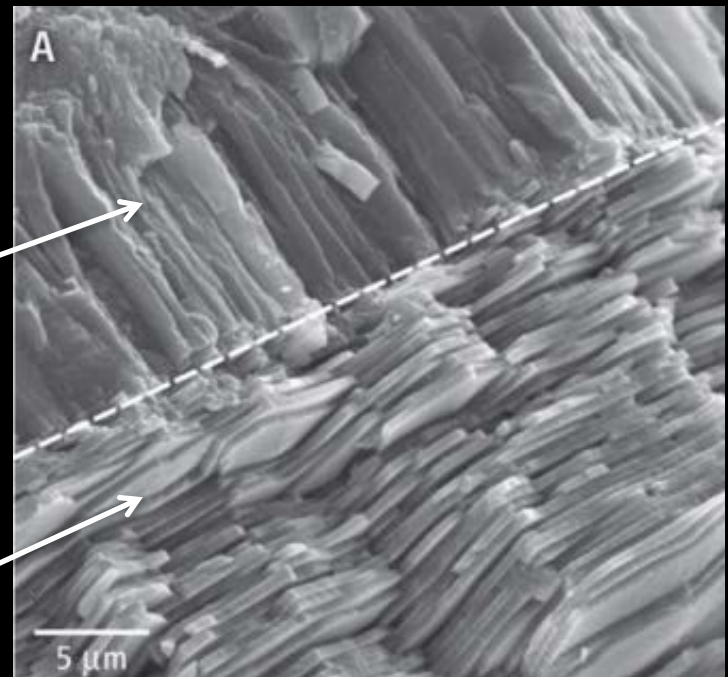
Nature as source of inspiration for engineering innovative solutions...



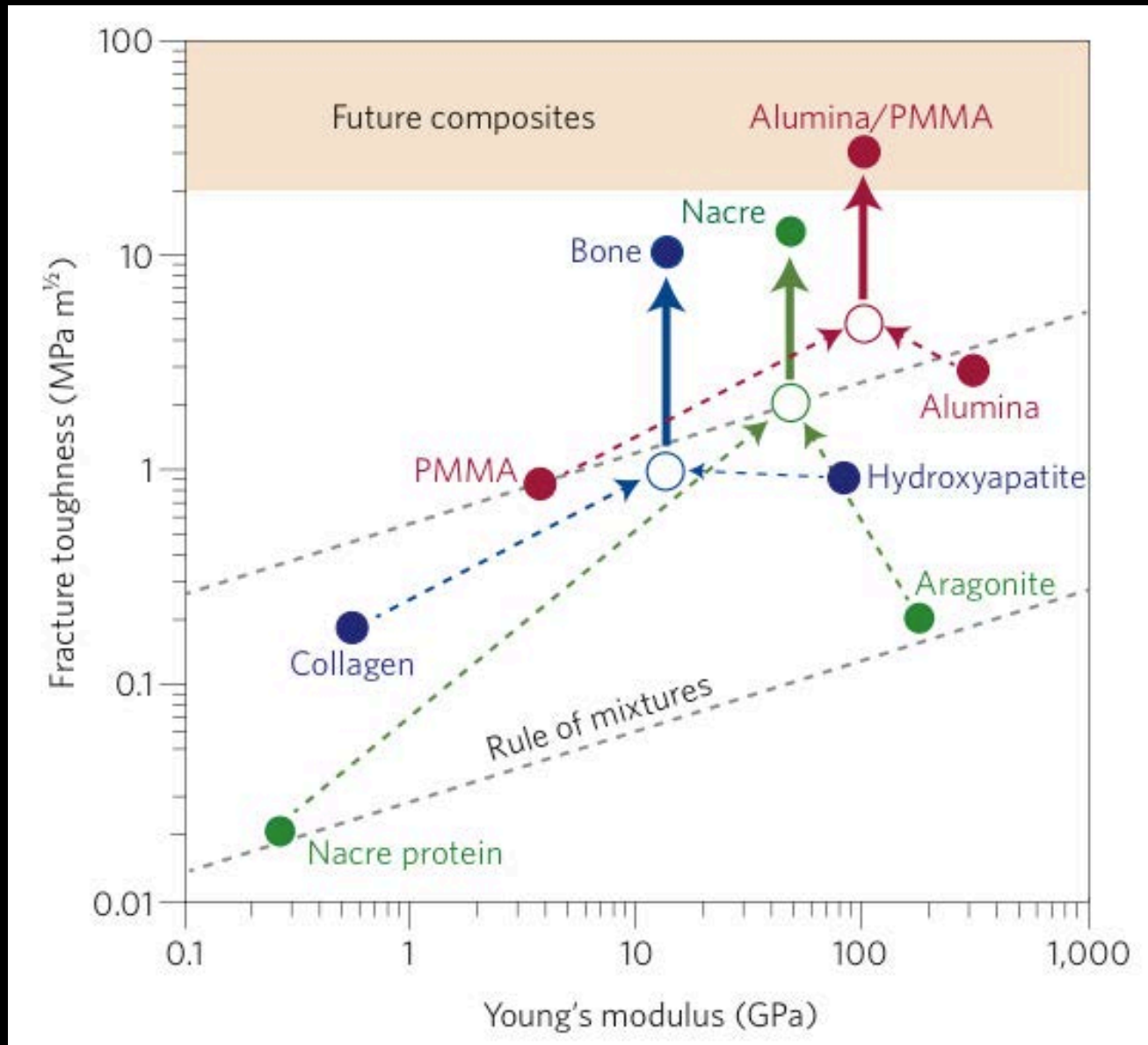
Fractured mollusk shell

Prismatic calcite

Nacre

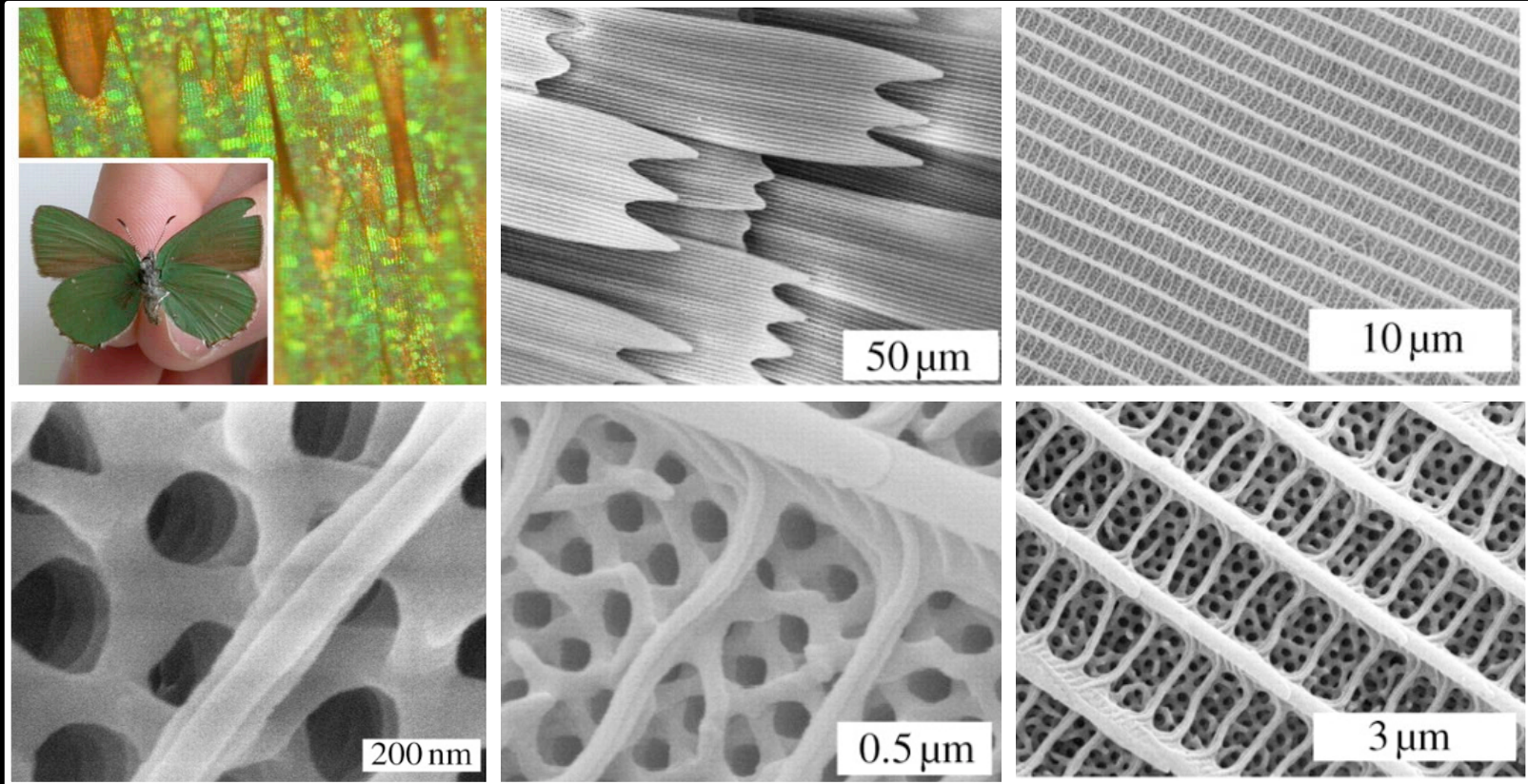


Nature as source of inspiration for engineering innovative solutions...



Adapted from Munch et al., Science, 322, 1516-1520 (2008) and Wegst et al Nat Mater 14, 23-36 (2015)

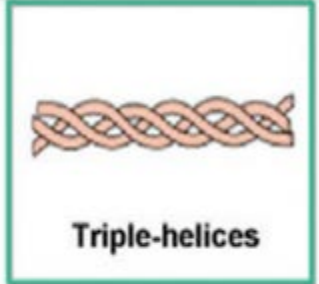

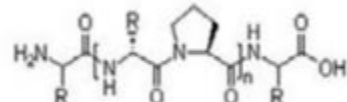
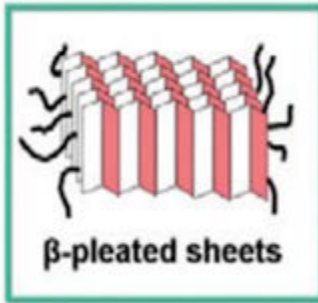

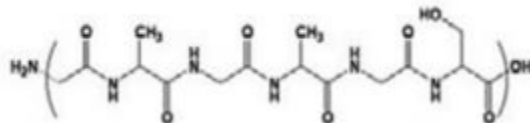
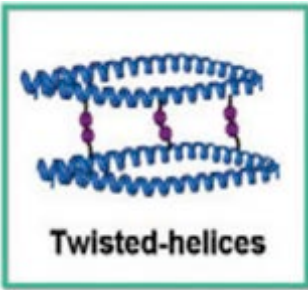

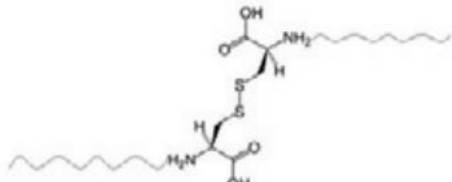
Nature as source of inspiration for engineering innovative solutions...



Structural biopolymers are the building materials of life – they realize a diversity of functions that provide structural support, locomotion and protection

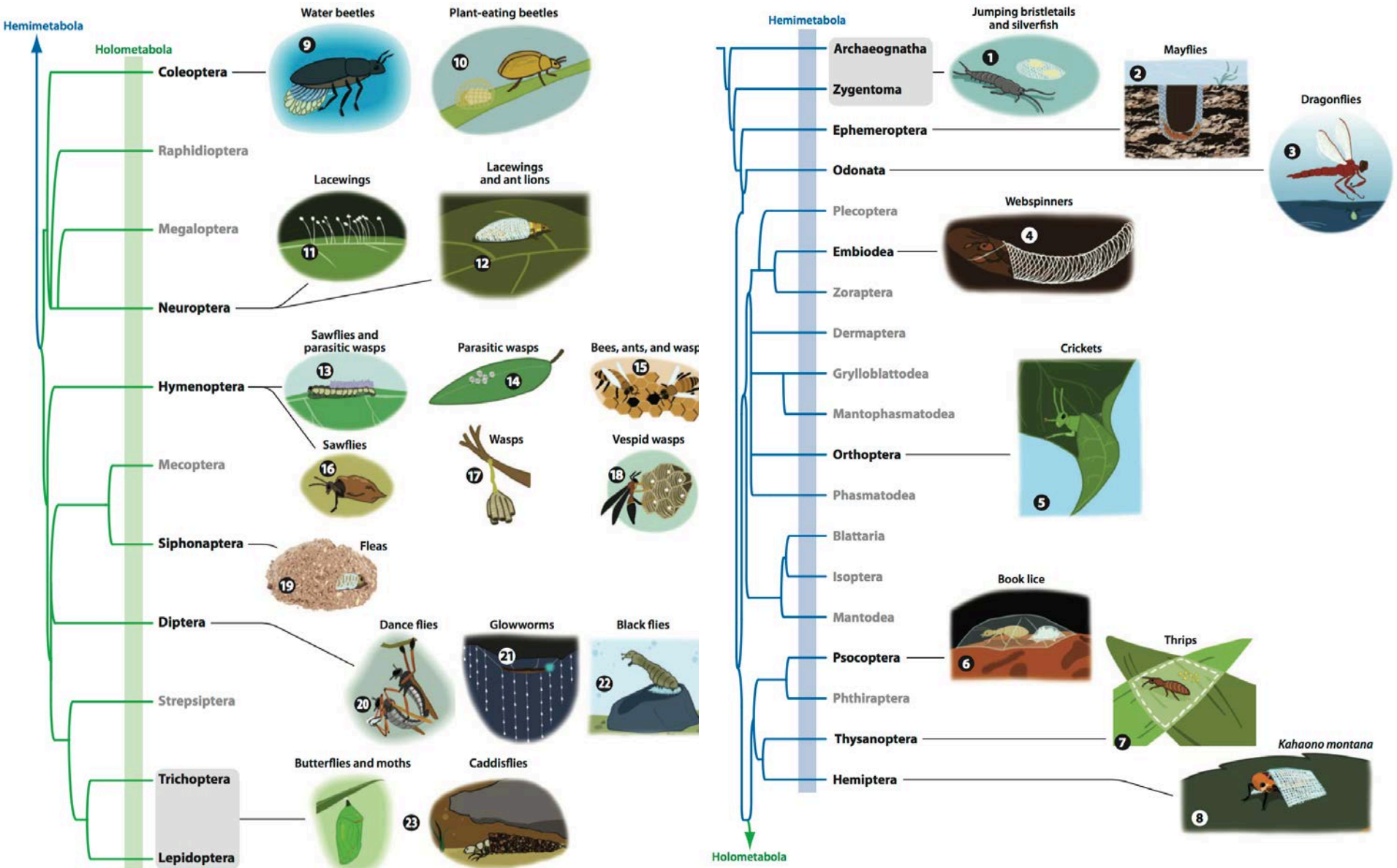
Key features:

- i. Simple material makeup developed to facilitate species survival
- ii. Materials efficiently created with low energy consumption
- iii. Simple processing conditions
- iv. Formed from a few distinct but abundantly available repeating material constituents

<p><u>Collagens</u> [GPX]_n</p>  <p>Triple-helices</p>	 
 <p>β-pleated sheets</p>	<p><u>Silks</u> [GAGAGS]_n</p>  
 <p>Twisted-helices</p>	<p><u>Keratins</u> α-[abcdef]_n or β-[GXG]_n</p>  



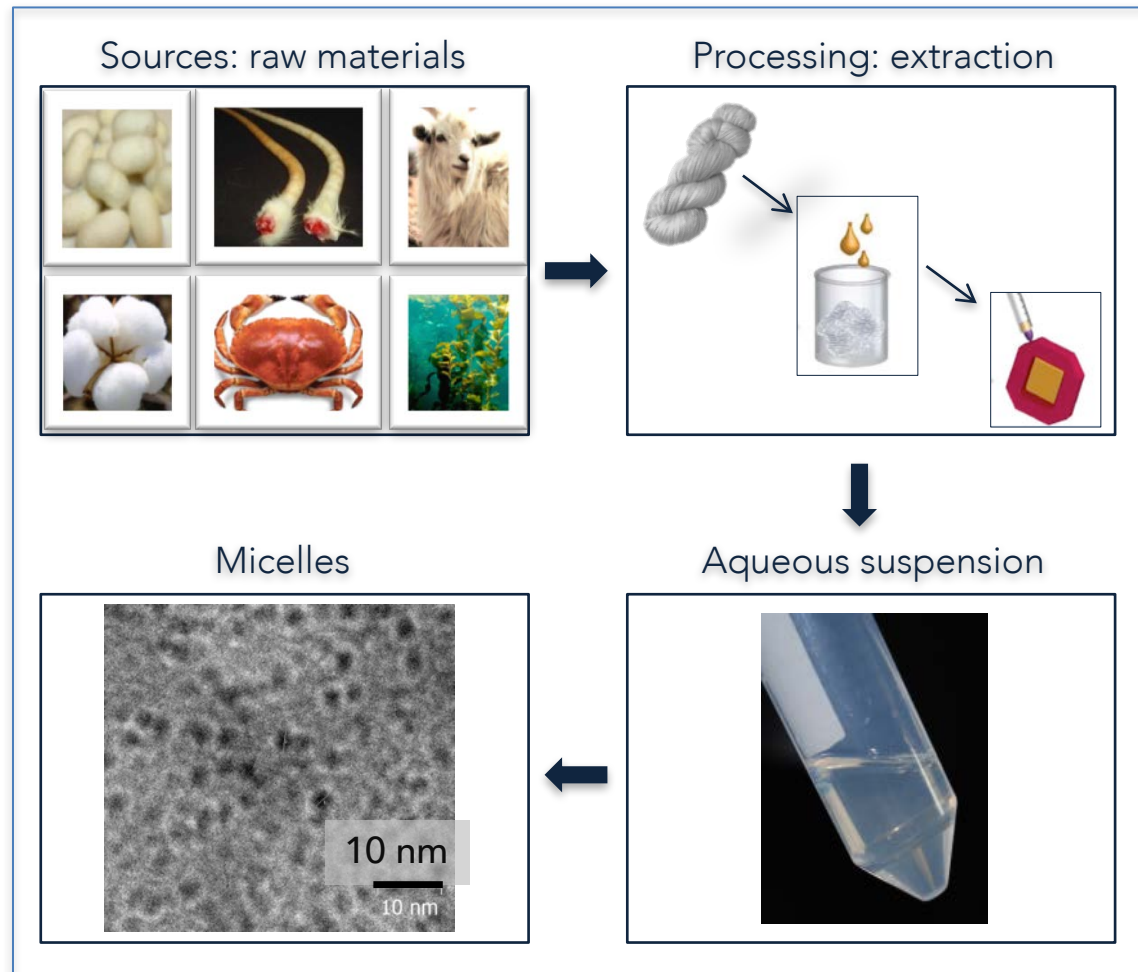
Insect Silk: One Name, Many Materials



Biopolymers can be regenerated to their molecular form – the reverse engineering process yields aqueous suspensions where the biomolecules are in a state similar to the extracellular one

Engineering design:

- i. Regeneration in aqueous solutions

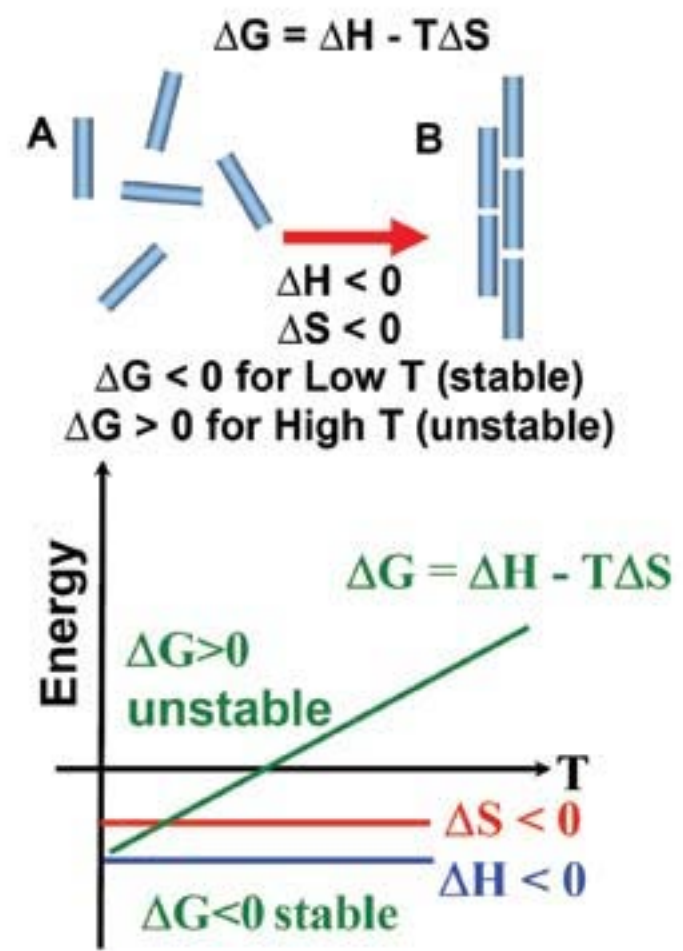


Assembly of silk materials

Key features:

- i. Low-energy processing
- ii. Mild environments
- iii. Self-assembly
- iv. Polymorphism

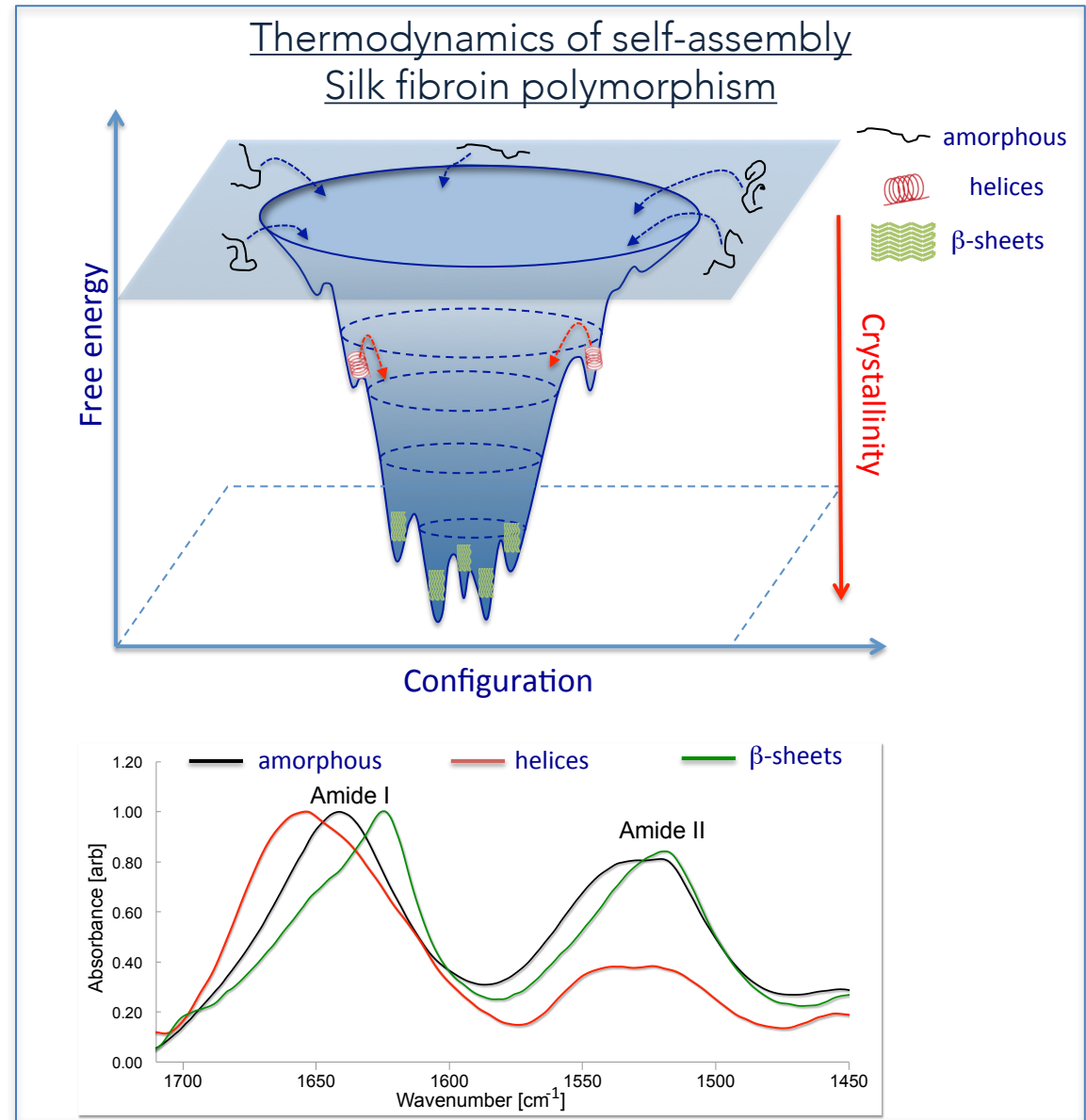
Thermodynamics of self-assembly



Assembly of silk materials

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Assembly of silk materials

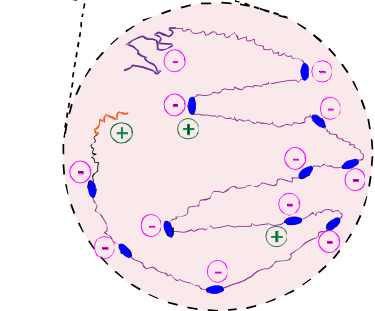
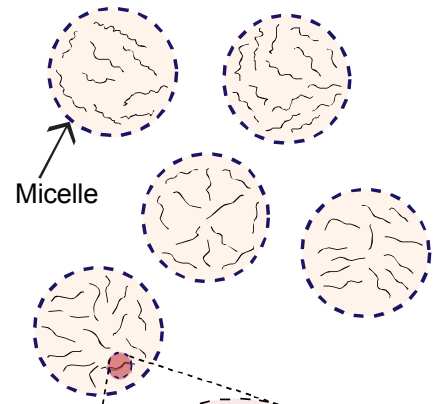
Key features:

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Silk fibroin self-assembly

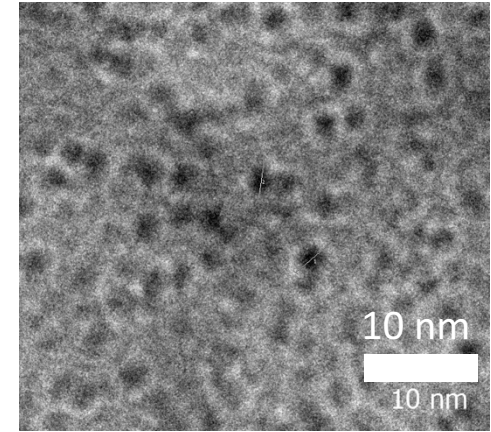
Silk solution

Solution state
Electrostatic repulsion



Silk fibroin heavy chain
in amorphous conformation
(no intermolecular interactions)

Regenerated fibroin solution



Marelli et al, PNAS 2017



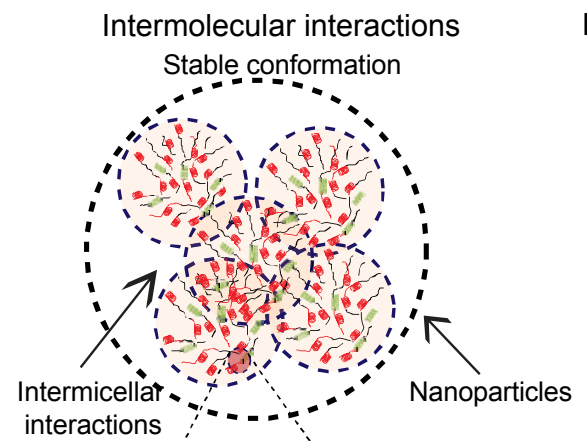
Assembly of silk materials

Key features:

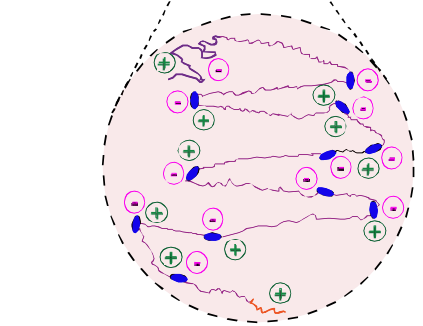
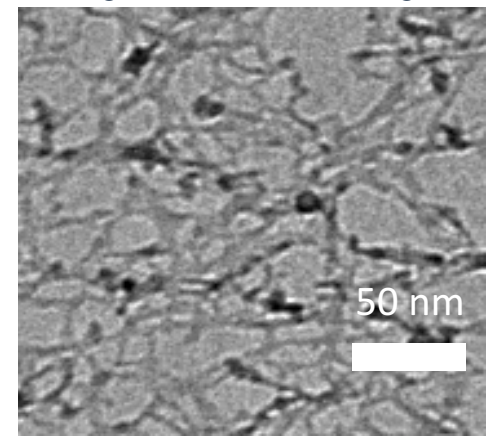
- i. Low-energy processing
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Silk fibroin self-assembly

Silk hydrogel



Regenerated fibroin gel



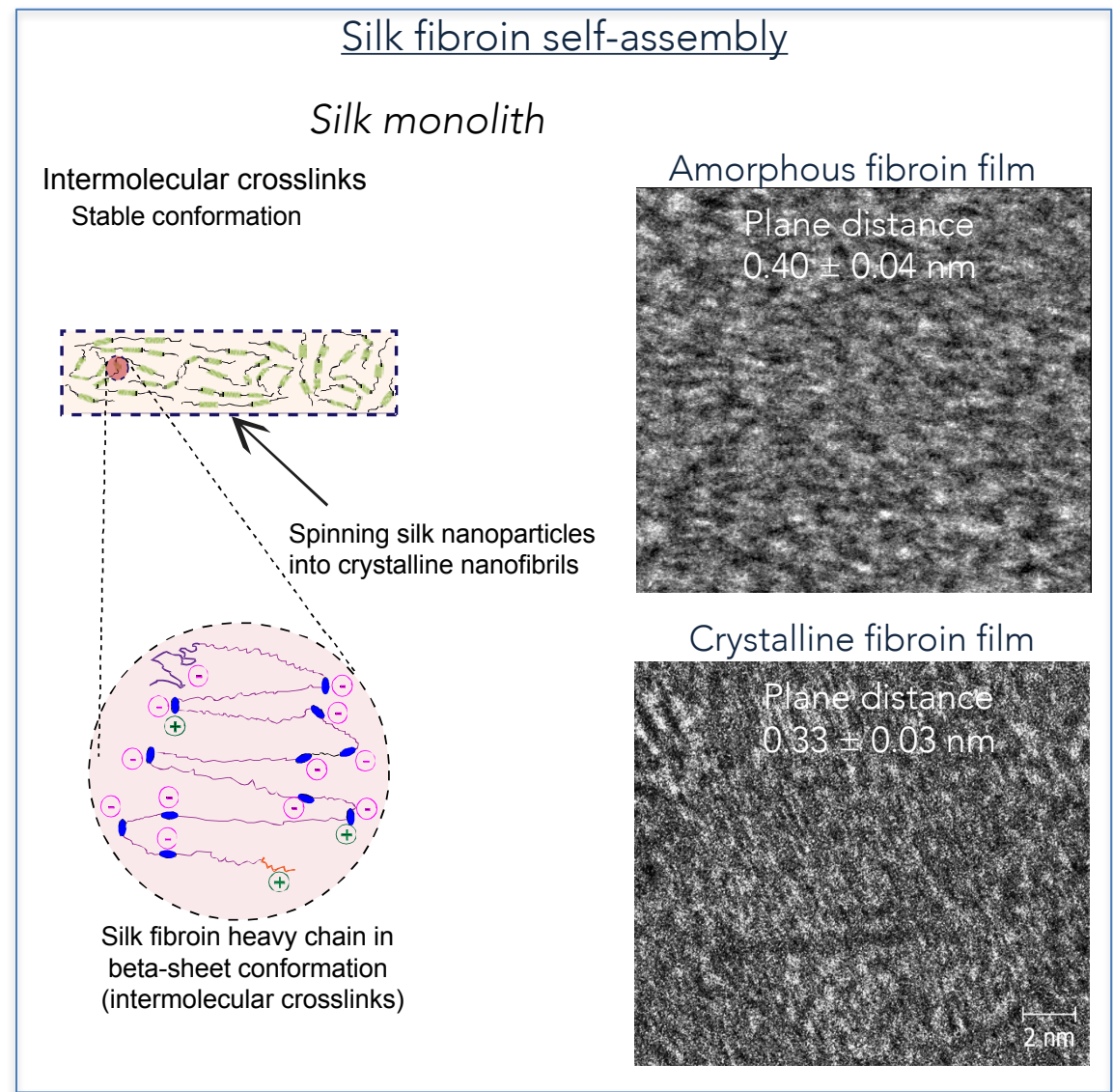
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Marelli et al, PNAS 2017

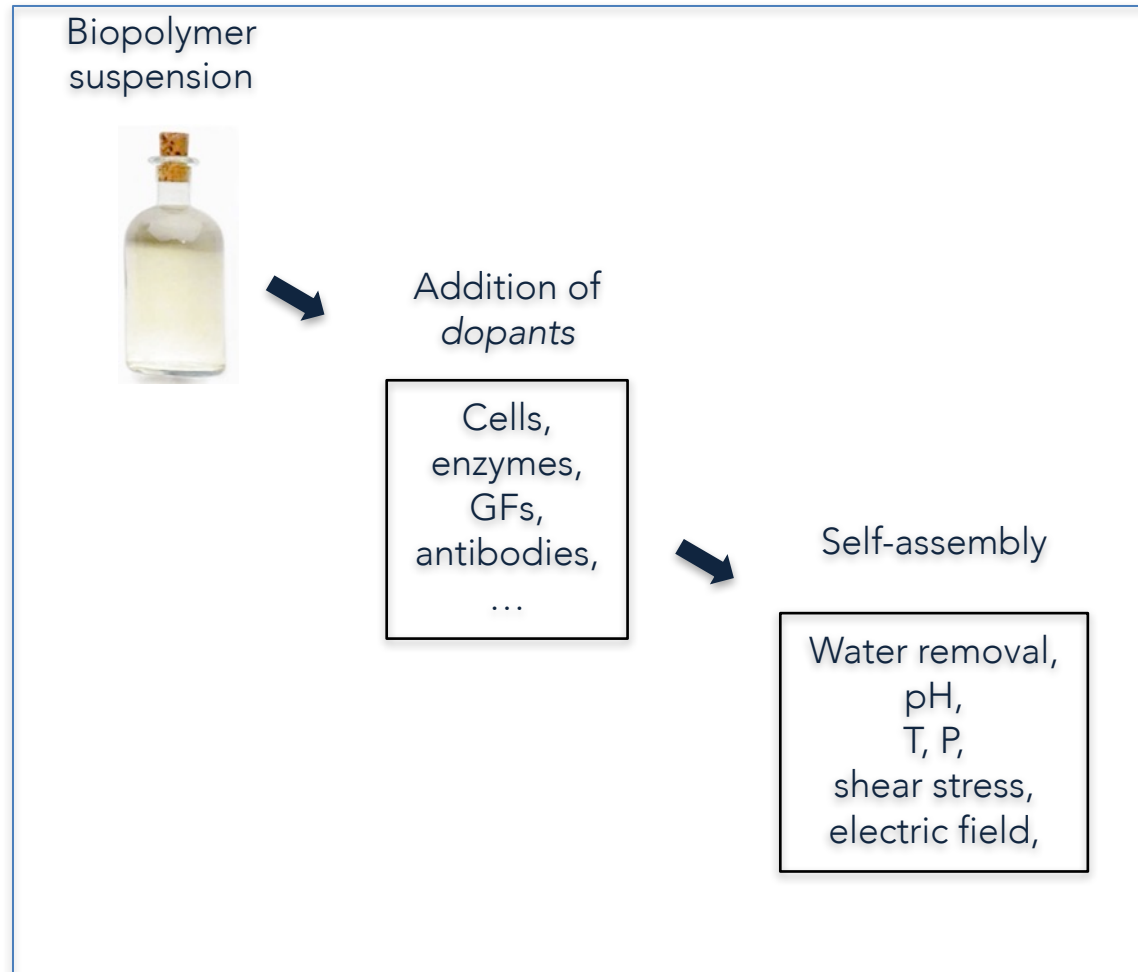


Biopolymers self-assembly is driven by modulating the molecular concentration in the suspension and environmental conditions – biological entities can be added at the point of self-assembly

Engineering design:

- i. Regeneration in aqueous *solutions*
- ii. Self-assembly in physiological conditions

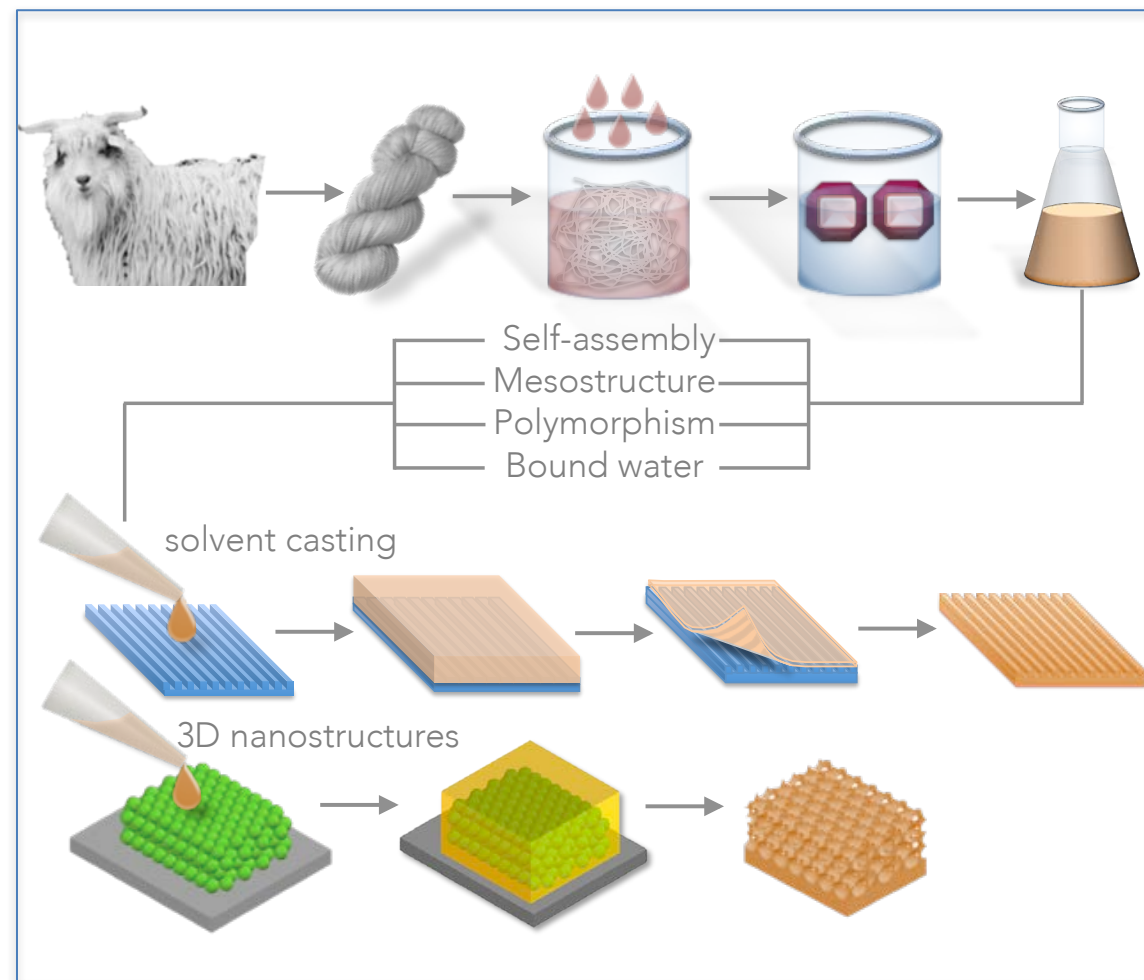
Key: addition of dopants enables the formation of biopolymers-based materials with programmable functions



Regenerated biopolymers can be used as fundamental building blocks to address unmet technological challenges in regenerative medicine and advanced manufacturing

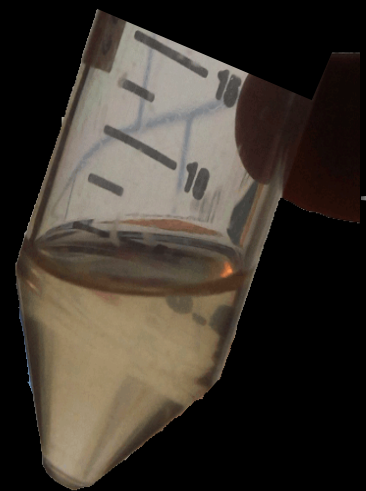
Key features:

- sustainable
- processed in water
- controlled degradation
- edible
- non-toxic
- implantable
- technological
- preserves bio-function

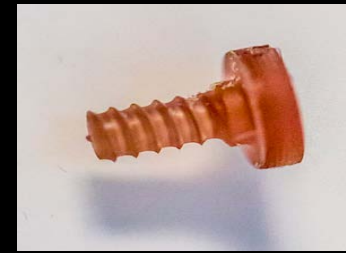


Forms and Functions

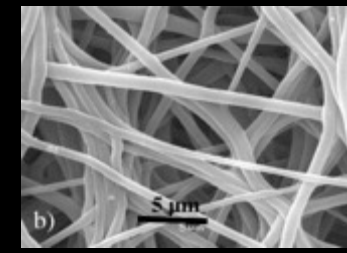
Material form: the silk protein can be fabricated in multiple formats that can be combined to orchestrate the engineering of materials with multiple functions in a single material format



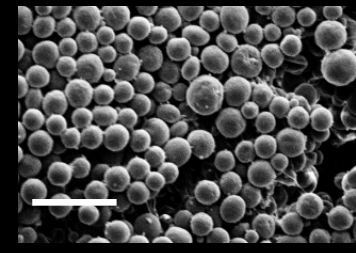
Monoliths



Fibres



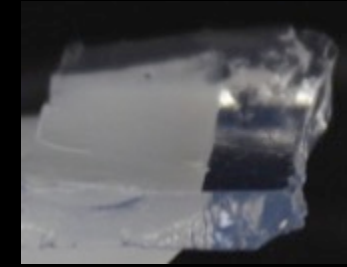
Particles



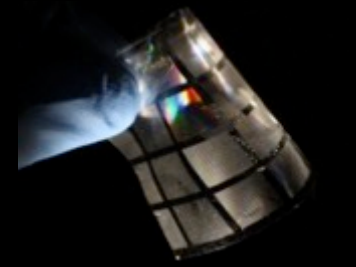
Tubes



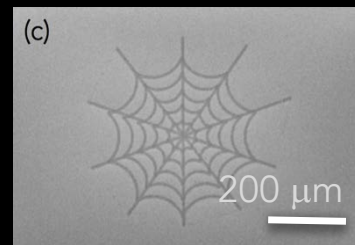
Gels



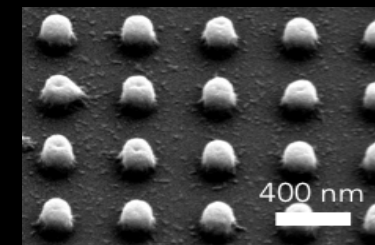
Films



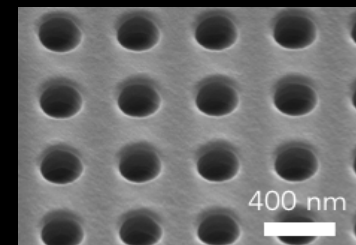
Inkjet printing



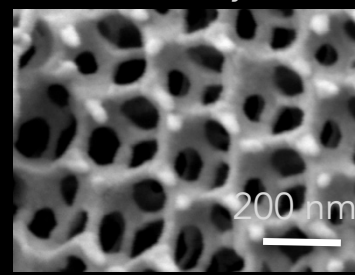
Nanopillars



Nanoholes



Photonic crystals



3d printing



Aerogels



Inkjet printing of silk fibroin: from printable forms to printable functions

Key features:

- i. Unprecedented versatility
- ii. Biotic/abiotic interface
- i. Biodegradable/compostable
- ii. Organic/inorganic interface

Silk fibroin polymorphism

(a) silk ink + biological dopant → functional silk ink → fill cartridge

(b) print 100 μm

(c) 2 mm

(d) 2 cm

(e) 2 cm

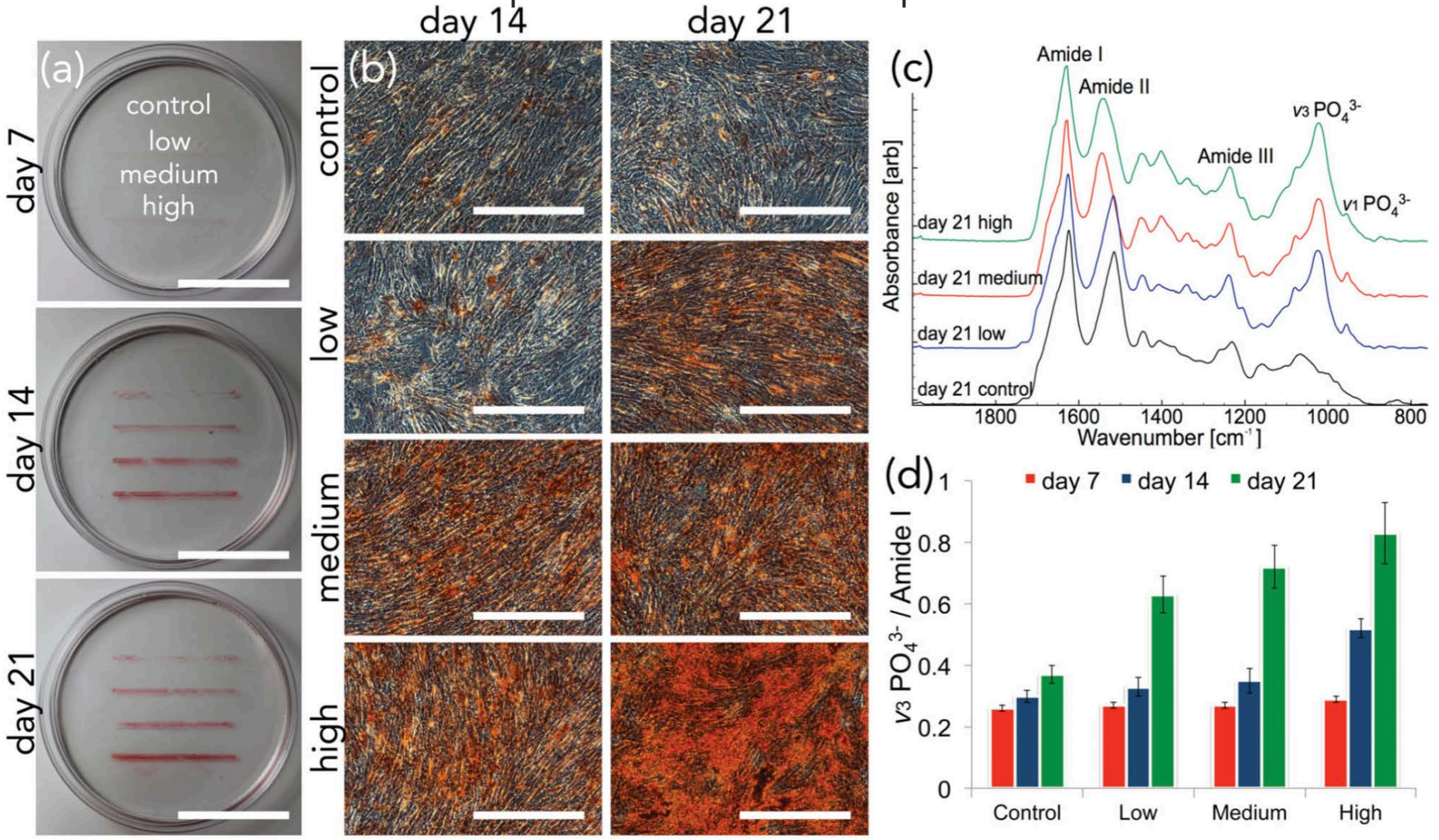
(f) 2 cm

Media coverage: **ADVANCED MATERIALS**, **CNN** (Silk 'microchip' heals you from the inside), **gizmag** (Silk-based functional inks put biosensor data on your fingertips), **la Repubblica il venerdì** (10 LUGLIO 2015)

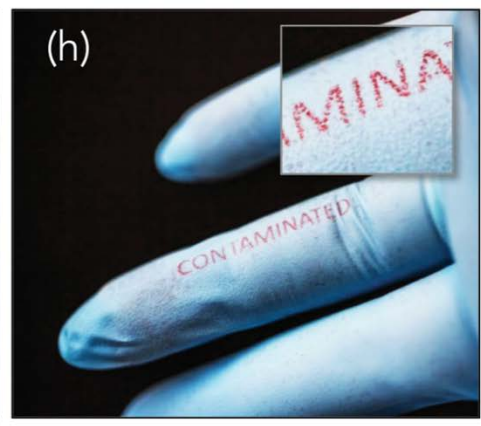
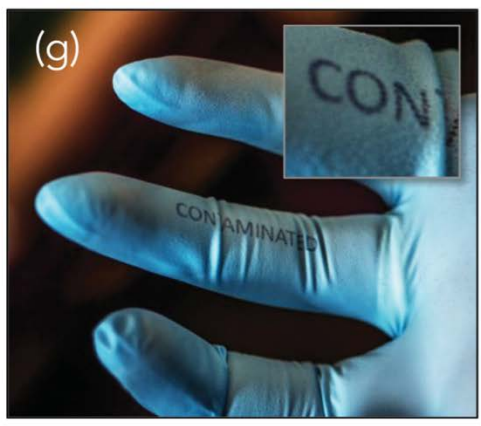
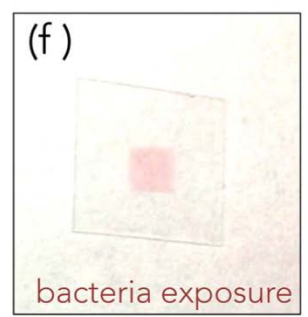
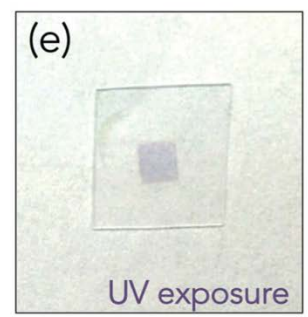
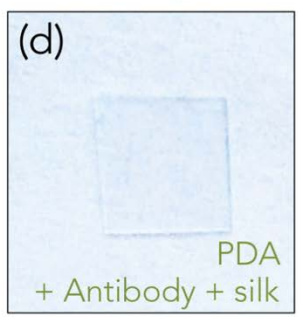
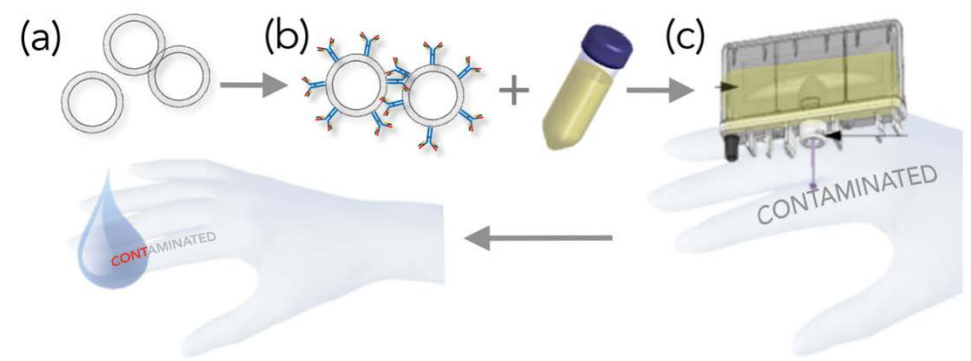
Marelli, Tao et al, Adv. Mater., 2015



IJP of silk fibroin: From printable forms to printable functions



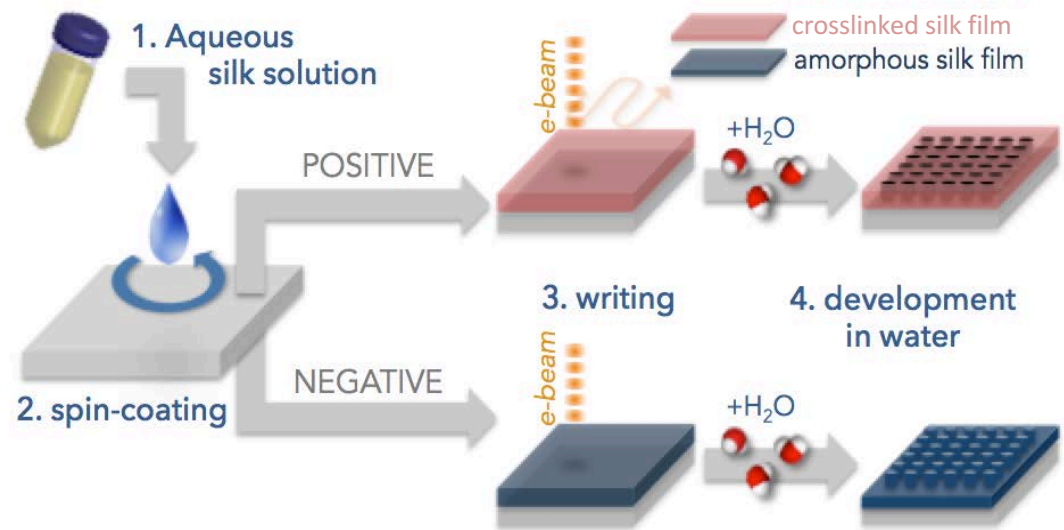
IJP of silk fibroin: From printable forms to printable functions



Nanofabrication of structural proteins can be achieved using top-down approaches as electron beam lithography

Engineering nanostructures:

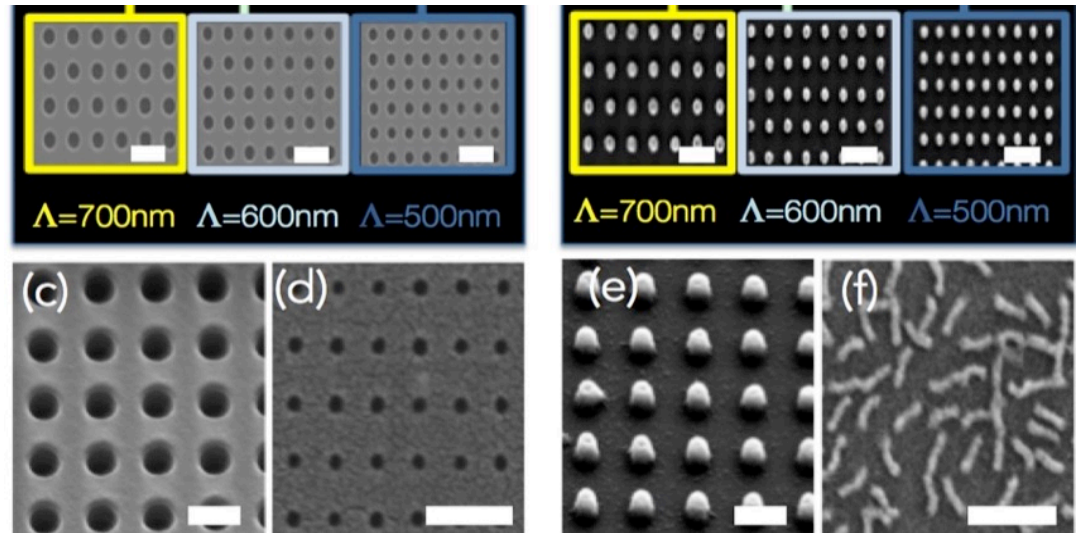
- i. Material final structure can be engineered with top-down strategies.
- ii. The process can be achieved completely 'out of the hood' with water-based 'chemistry'
- iii. Sub-10 nm resolution can be achieved both as positive or negative resist



Nanofabrication of structural proteins can be achieved using top-down approaches as electron beam lithography

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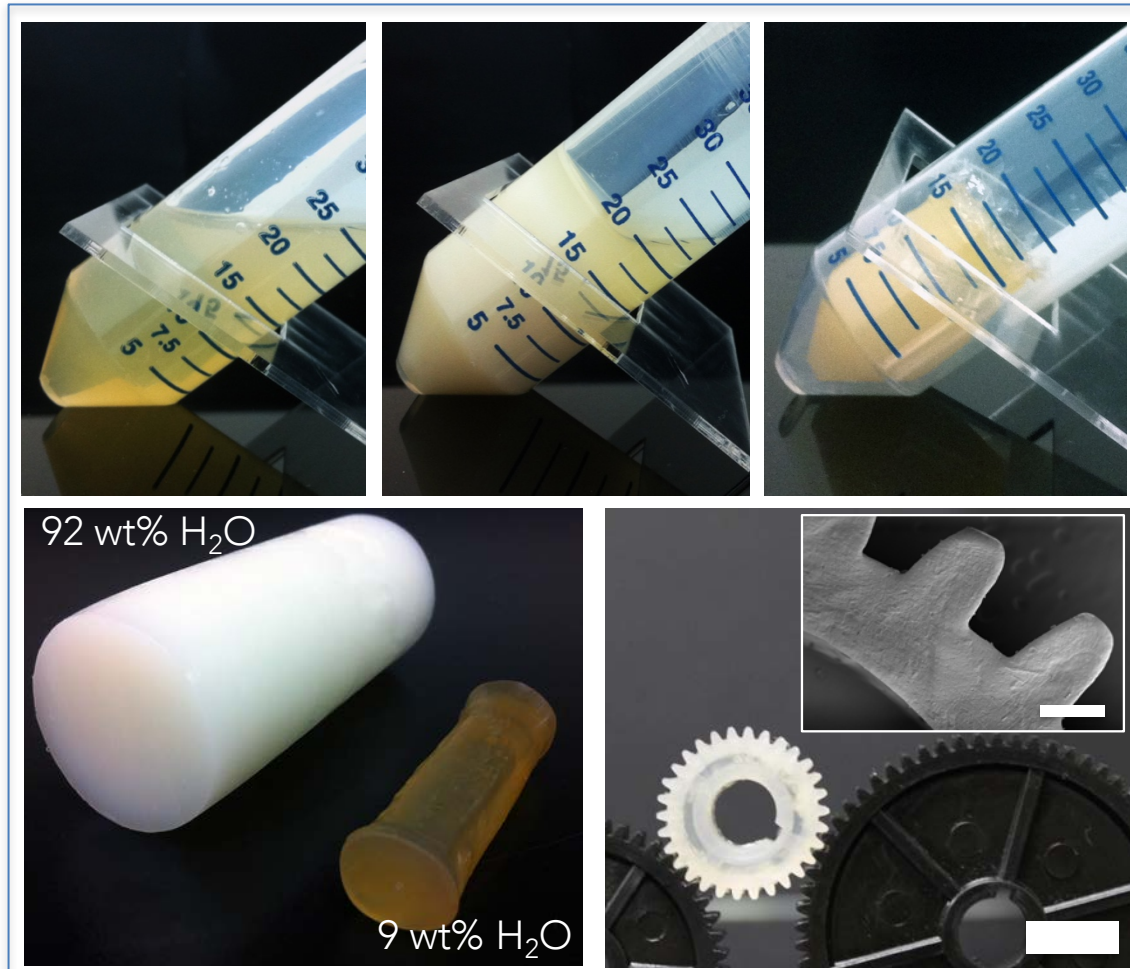
- i. Material final structure can be engineered with top-down strategies.
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Biofabrication of structural proteins in advanced materials can be achieved by directing and templating self-assembly and by modulating polymorphism, bound water and molecular weight

Engineering structures:

- i. The material final structure can be engineered with bottom-up approaches.
- ii. Templating self-assembly allows to obtain complex shapes with no need for 'machining'
- iii. Alternatively, simple biopolymers blocks (prism or cylindrically-shaped) may be fabricated and then machined to the final shape

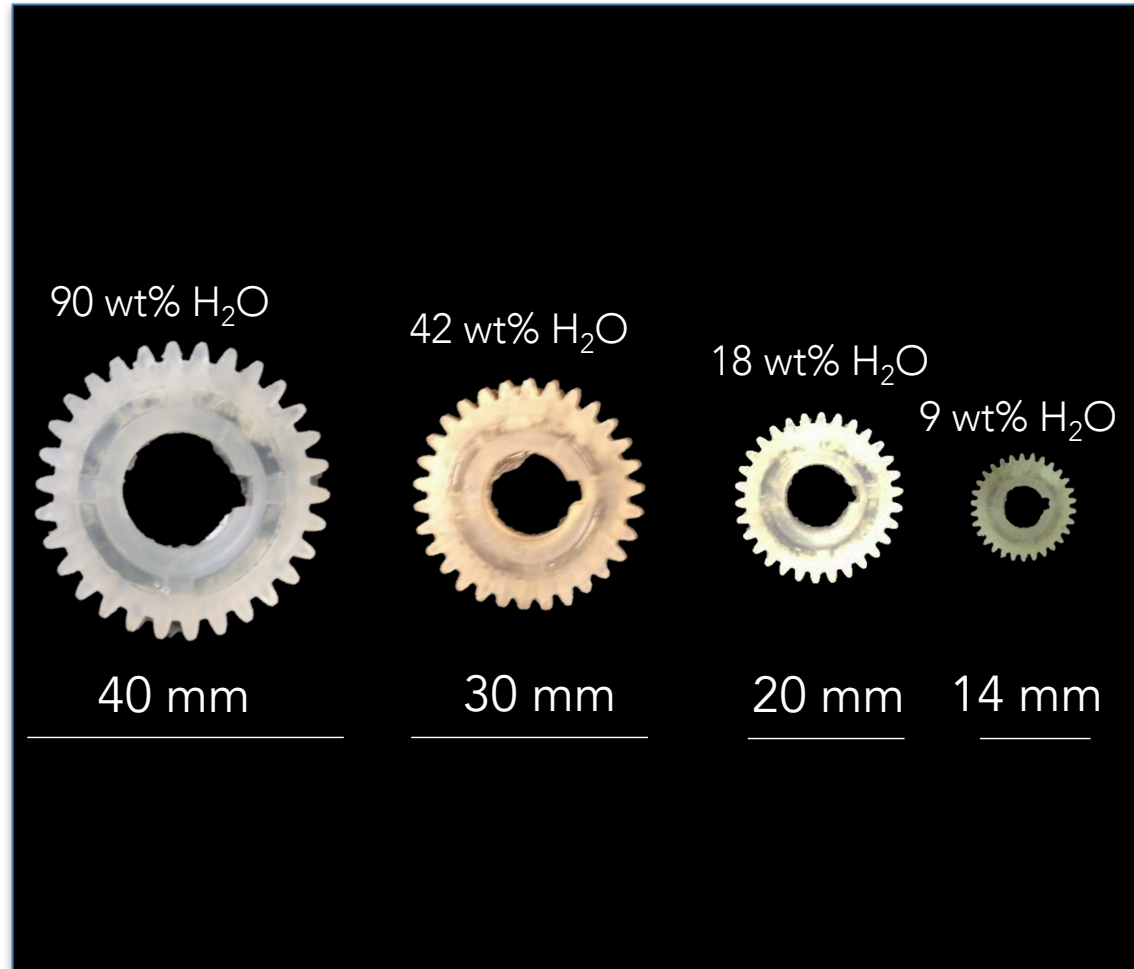


Biofabrication of structural proteins in advanced materials can be achieved by directing and templating self-assembly and by modulating polymorphism, bound water and molecular weight

Engineering structures:

Fabrication of three dimensional silk fibroin complex structures (e.g. gears) of defined dimensions by molding process.

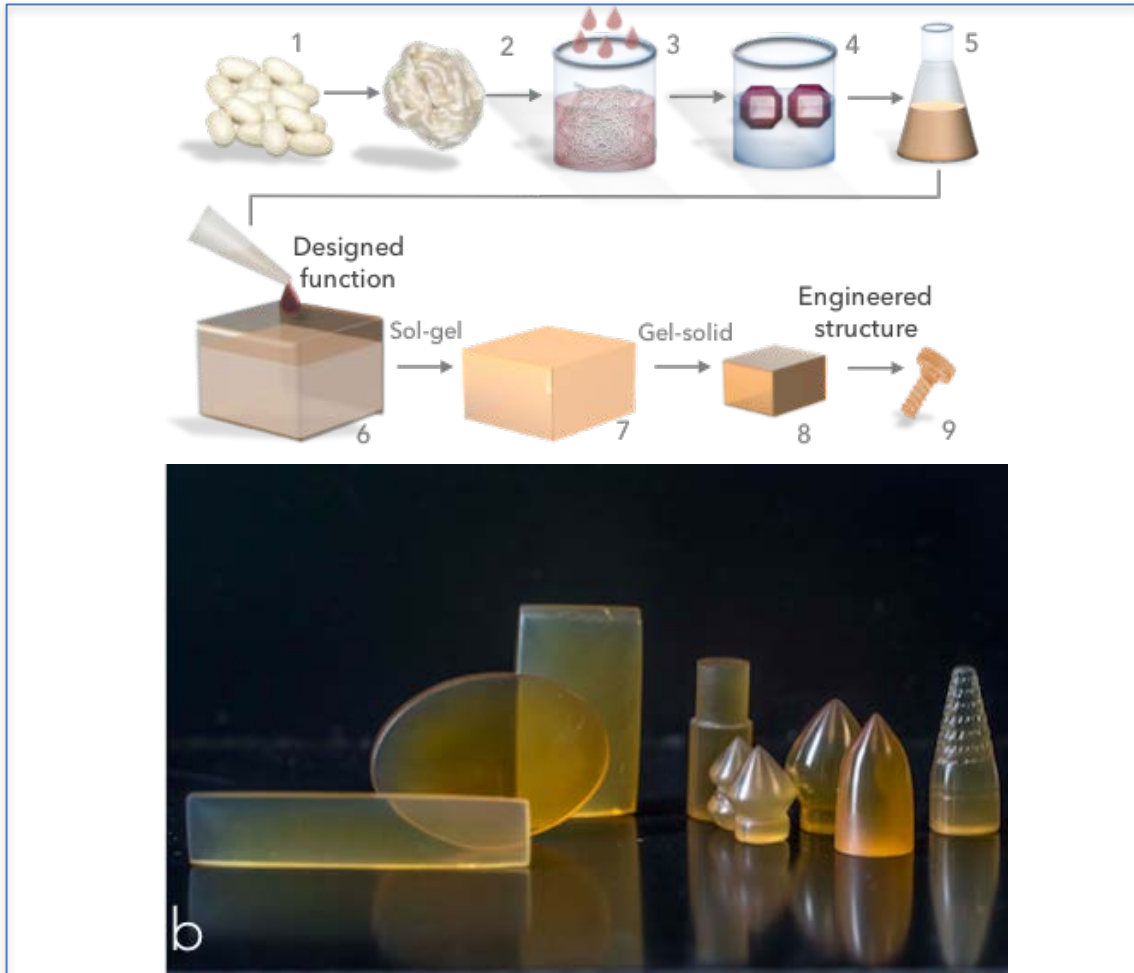
Designing the original master has to take into account for shrinkage in the gel-solid processing step, due to evaporation of the mold.



Unexpected functions can be achieved by doping biopolymer structures with water-soluble molecules that impart 'orthogonal' properties to the final material

Designed functions:

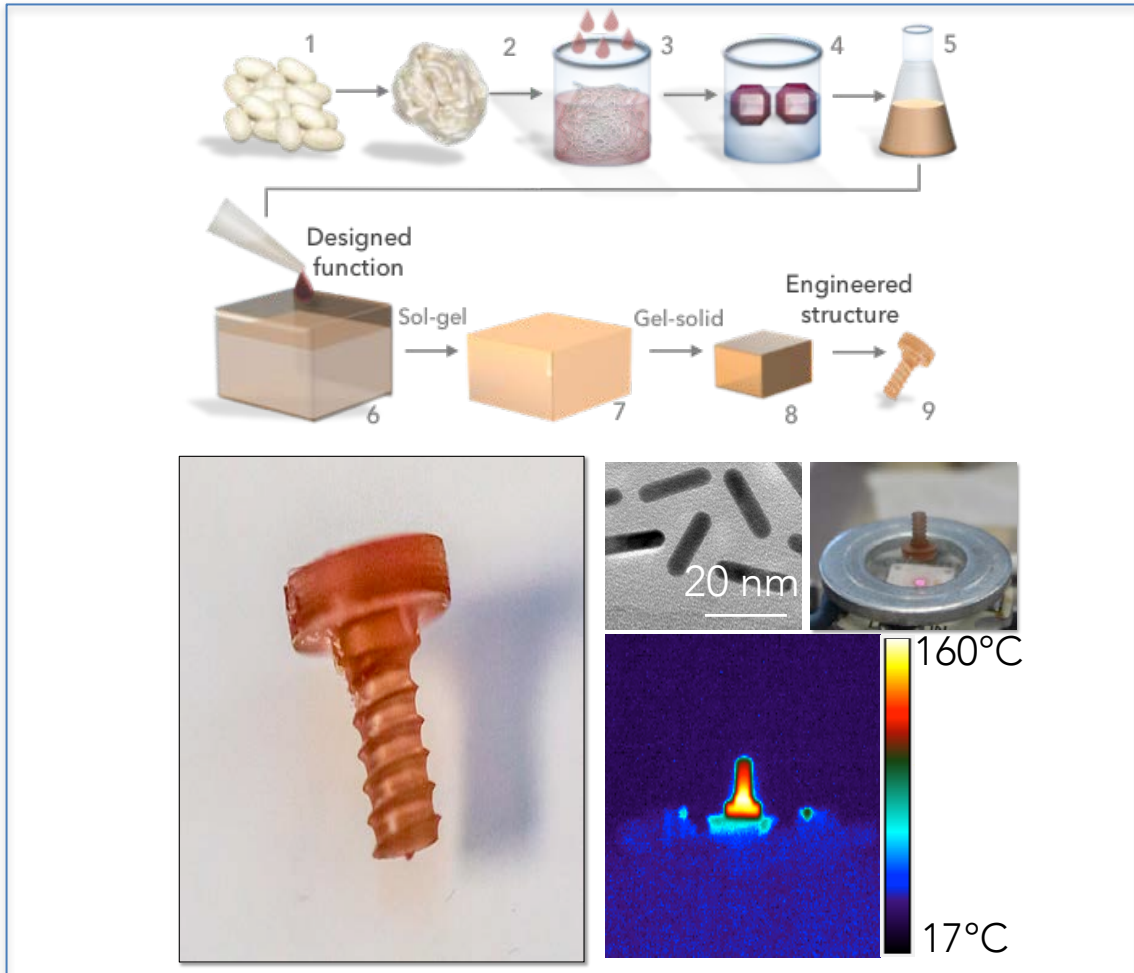
- i. New functionalities may be achieved by fabricating 'hybrid materials' via doping at the point of material self-assembly



Unexpected functions can be achieved by doping biopolymer structures with water-soluble molecules that impart 'orthogonal' properties to the final material

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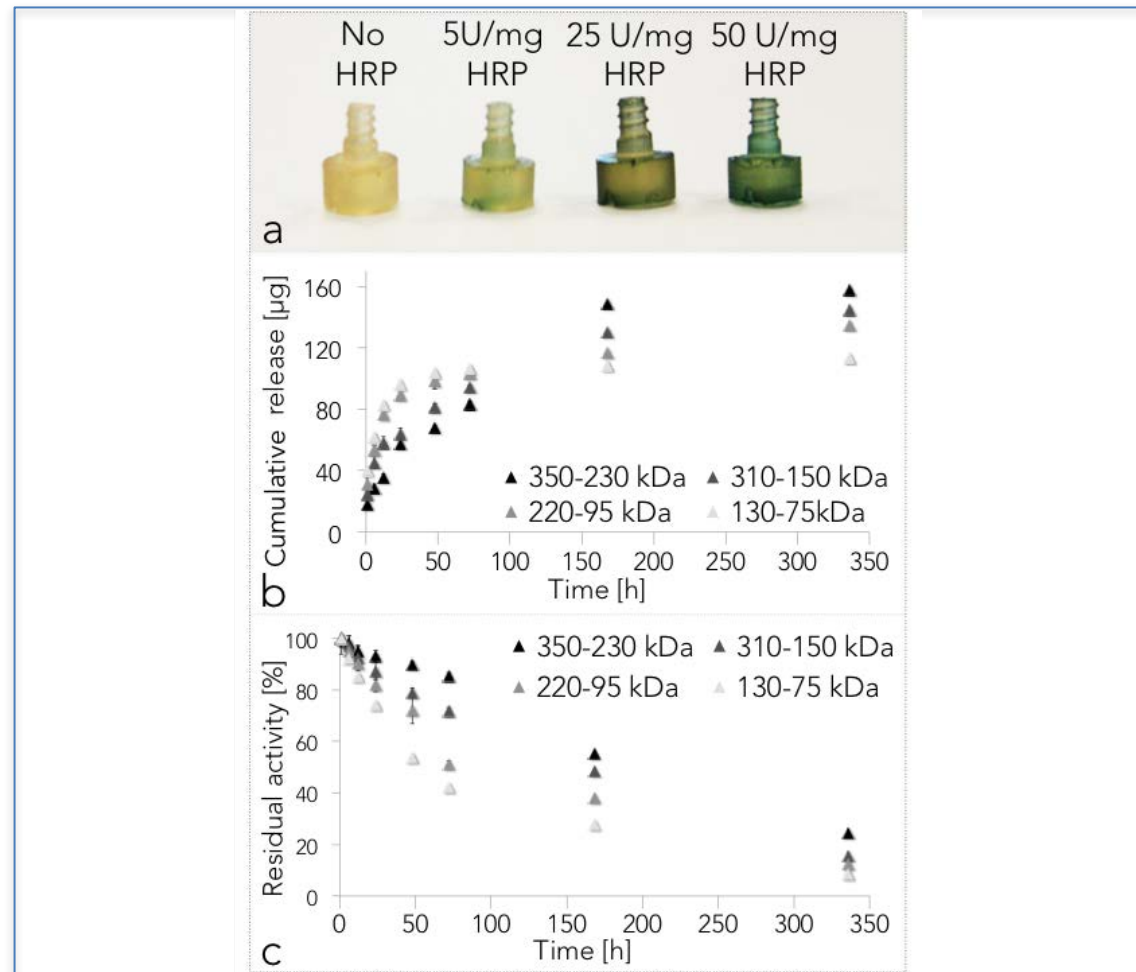
- i. New functionalities may be achieved by fabricating 'hybrid materials' via doping at the point of material self-assembly
- ii. Gold nanorods with tailorable plasmonic resonances may be incorporated, yielding mechanical components that heats up when irradiated with visible (red) and near-IR light.



Unexpected functions can be achieved by doping biopolymer structures with water-soluble molecules that impart 'orthogonal' properties to the final material

Designed functions:

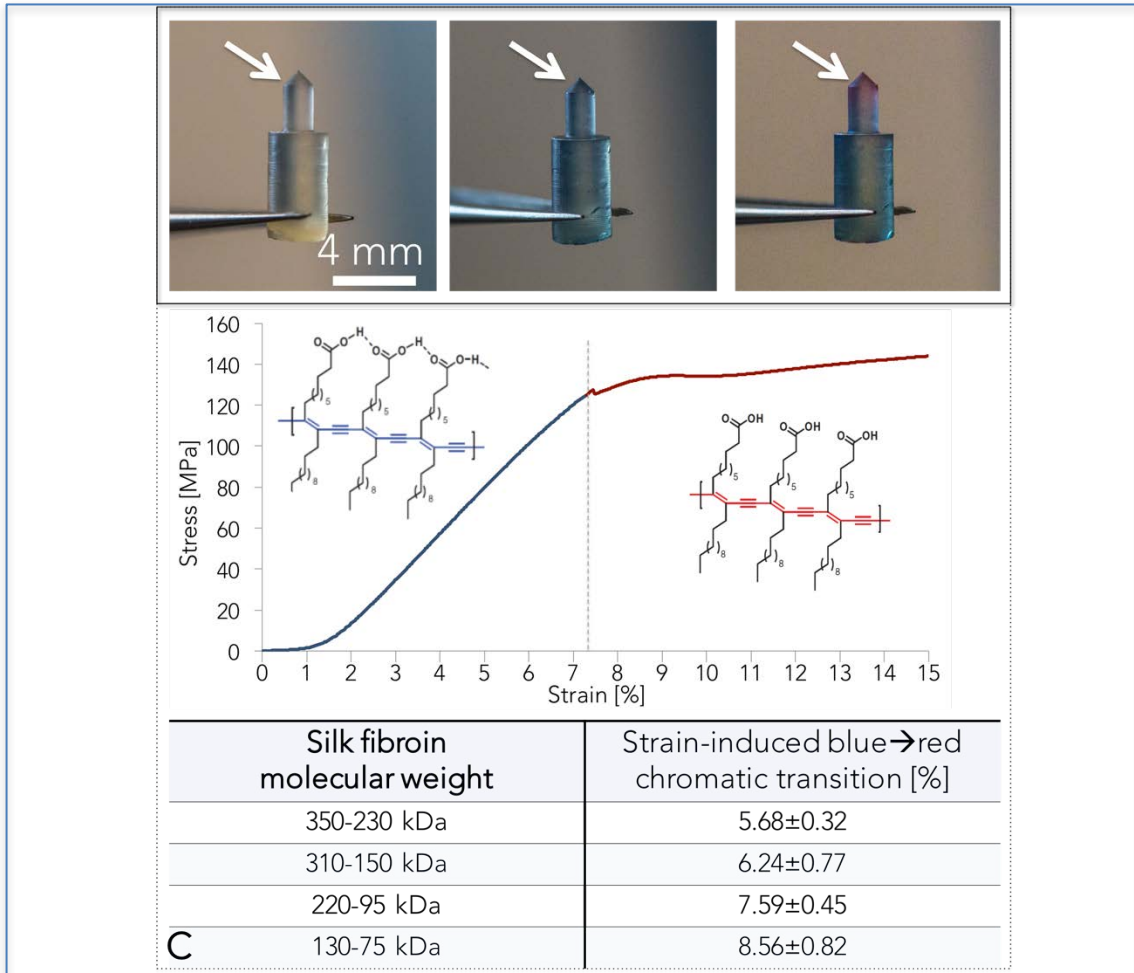
- i. New functionalities may be achieved by fabricating 'hybrid materials' via doping at the point of material self-assembly
- ii. Engineered silk fibroin screws with biological functions - horseradish peroxidase can be incorporated in engineered silk screws to impart catalytic activities to the material.



Unexpected functions can be achieved by doping biopolymer structures with water-soluble molecules that impart 'orthogonal' properties to the final material

Designed functions:

- i. New functionalities may be achieved by fabricating 'hybrid materials' via doping at the point of material self-assembly
- ii. Polymers that change in color when exposed to mechanical stresses may be incorporate to design mechanical components that 'sense' when they are plastically deformed (i.e. yield point)

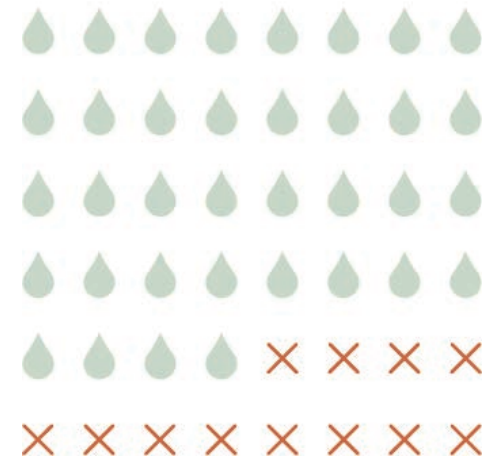


WITH 9B MOUTHS TO FEED BY 2050, WE HAVE TO GET BUSY NOW

Food loss and its intersection with food security

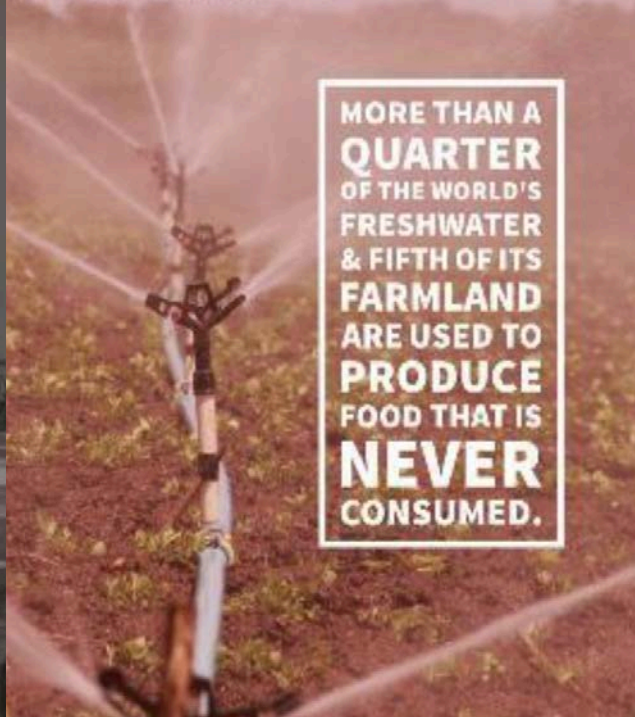


One quarter of global freshwater consumption is used producing food that is never eaten.





**THE FOOD
LOST EVERY
YEAR COULD
FEED AN ESTIMATED
1.6 BILLION
PEOPLE GLOBALLY.**



**MORE THAN A
QUARTER
OF THE WORLD'S
FRESHWATER
& FIFTH OF ITS
FARMLAND
ARE USED TO
PRODUCE
FOOD THAT IS
NEVER
CONSUMED.**



**Each year 1/3 of all food
produced for human
consumption - 1.3 billion
tons - never makes it from
farmers to consumers.**



**53 MILLION TONS
OF FOOD ARE
SENT TO LANDFILL
IN THE US EVERY
YEAR.**

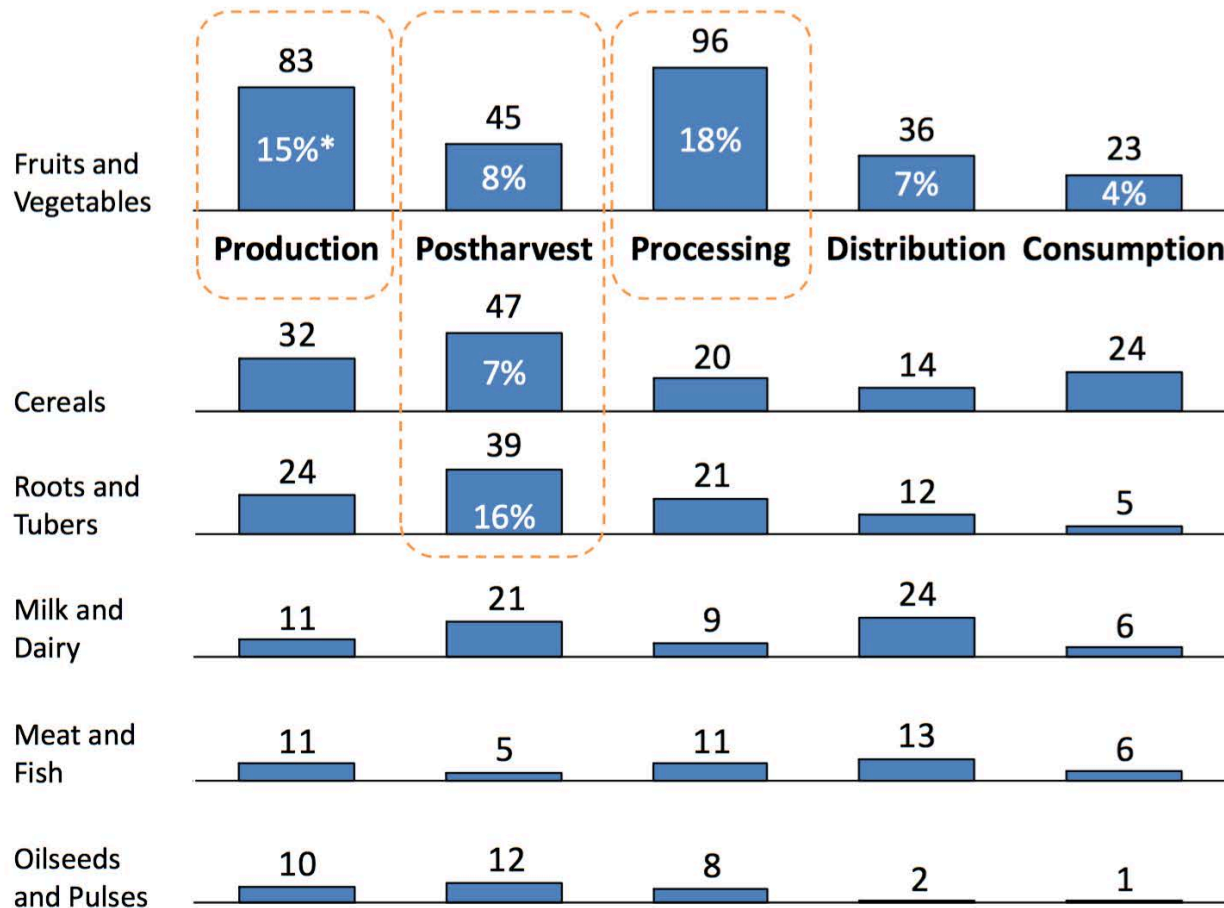
**FOOD LOSS RESULTS
IN 15% INCOME
REDUCTION
FOR 470 MILLION
SMALLHOLDER FARMERS.**



**AMERICAN CONSUMERS,
BUSINESSES, AND FARMS
WASTE 40% OF
THE FOOD GROWN AND
PRODUCED FOR
CONSUMPTION
EVERY YEAR.**

Amount of wastage in developing countries, millions of metric tons and as % of production¹

The largest sources of loss in developing countries are in fruits and vegetables and the postharvest storage of cereals, roots, and tubers.



Primary Root Causes

Fruits and Vegetables:

- Production: 15%* is lost through manual harvest, bad weather during the harvest season, and premature harvest due to cash constraints.
- Postharvest: 8% is lost, mainly due to bruising or damage from improper packaging or handling, lack of cold storage in warm and humid climates, and seasonality that yields surpluses.
- Processing: 18% is lost due to high seasonality and poor storage, together lowering incentives to build processing capacity that meets total demand.

Cereals:

- Postharvest: 7% is lost due to improper storage, attributable to poor hygiene, pest infestation or bumper harvests beyond capacity.

Roots and Tubers:

- Postharvest: 16% is lost, mainly due to lack of cold storage in warm climates and distance to market.

*Note: Percentages listed are share of total category production in developing countries.

News

The end of the mouldy fruit bowl? Scientists discover microscopic silk covering to keep food fresh

LIFE | IDEAS | R AND D

A Silky Solution to the Problem of Wasted Food?

By DANIEL AKST

May 19, 2016 2:27 p.m. ET

Food waste is a big problem, and produce is particularly vulnerable. Largely due to spoilage, 40-50% of the world's fruit and vegetable output is wasted, according to a U.N. estimate, along with a great deal of labor, water and energy.

Silk Fibroin as Edible Coating for Perishable Food Preservation

NEWSFEED

This One Surprising Trick Might Keep Fruit Fresh for Longer

This One Surprising Trick Might Keep Fruit Fresh for Longer

Olivia B. Waxman @OBWax | May 6, 2016

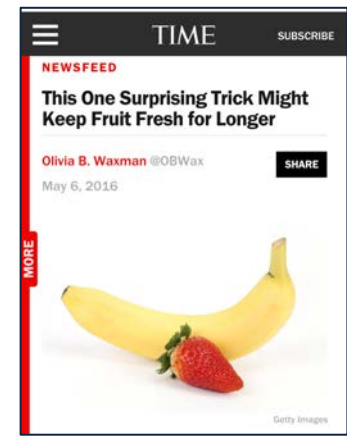
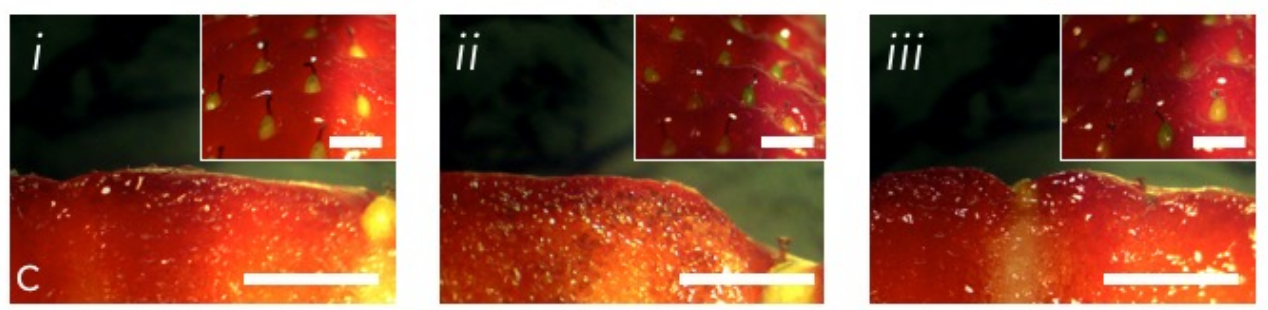
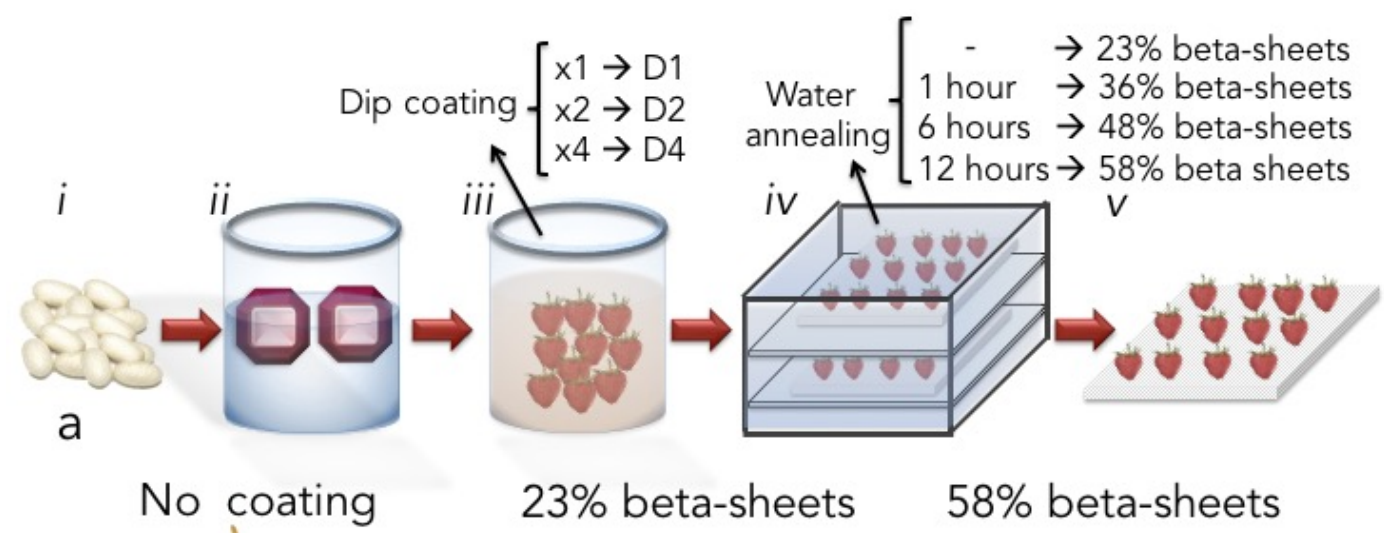


The food preserver

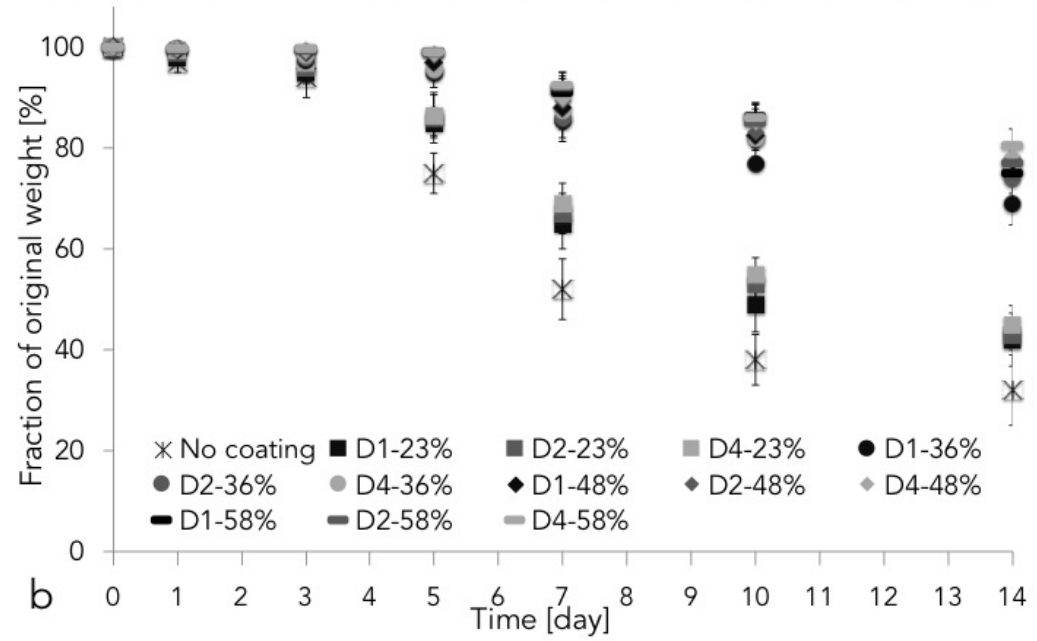
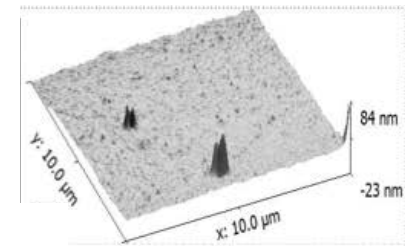
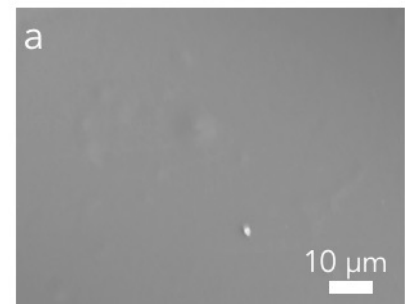
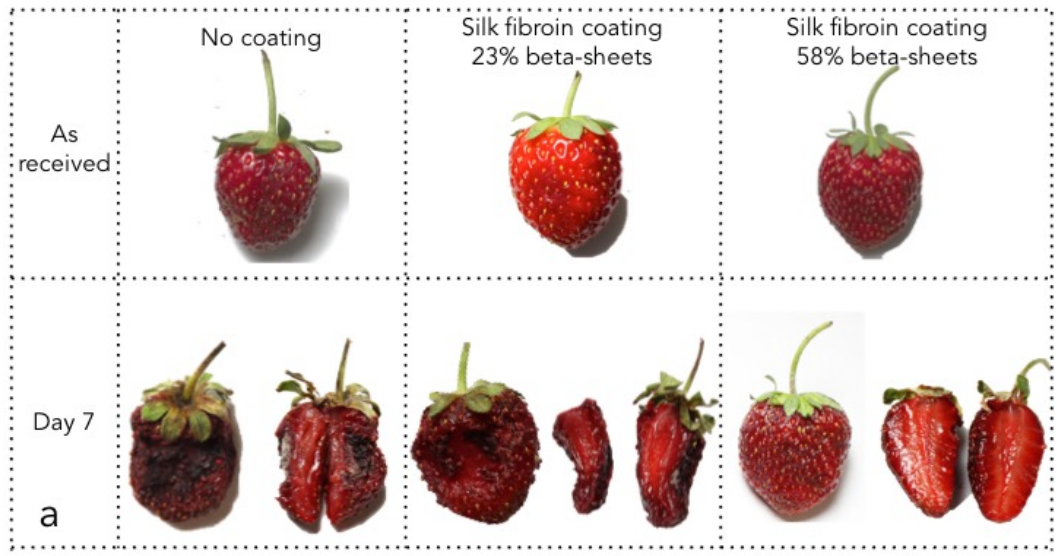


Could silk be used to preserve our fruit in the future?

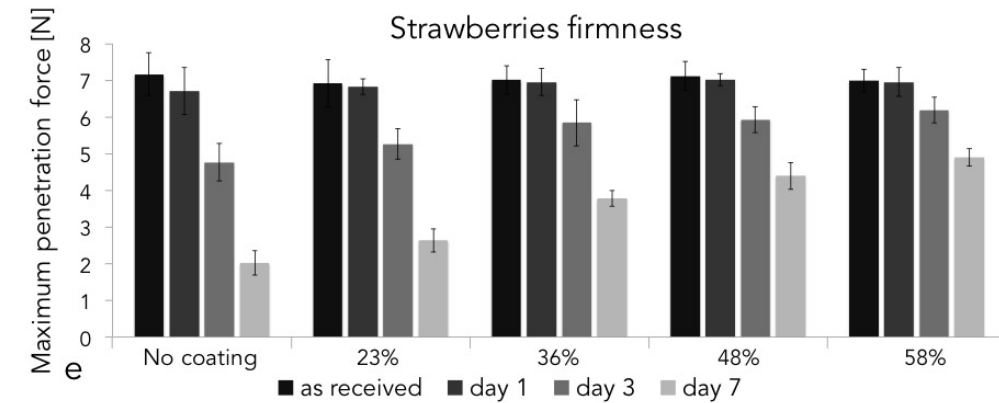
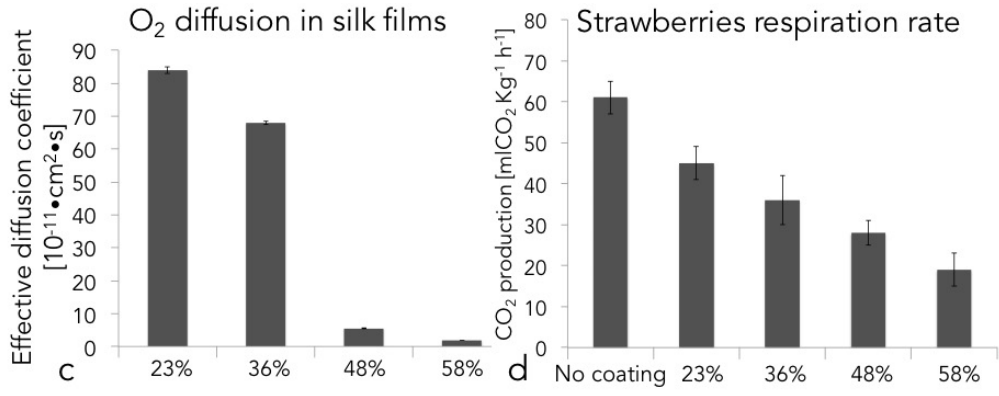
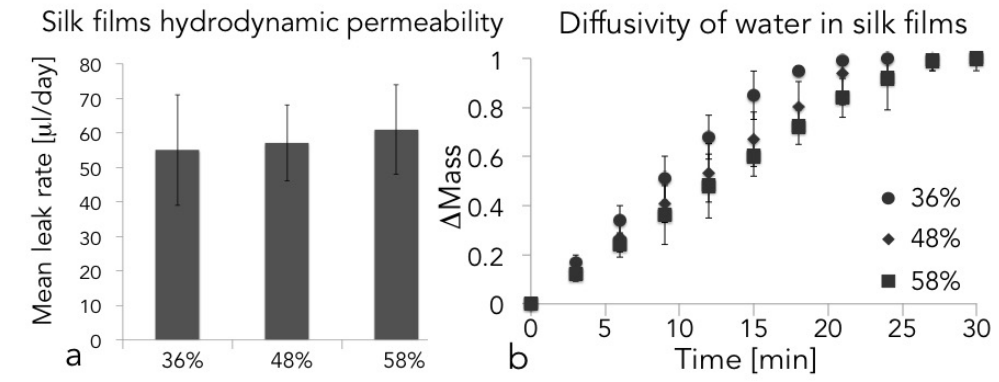
Edible coating for perishable food preservation



Edible coating for perishable food preservation



Edible coating for perishable food preservation



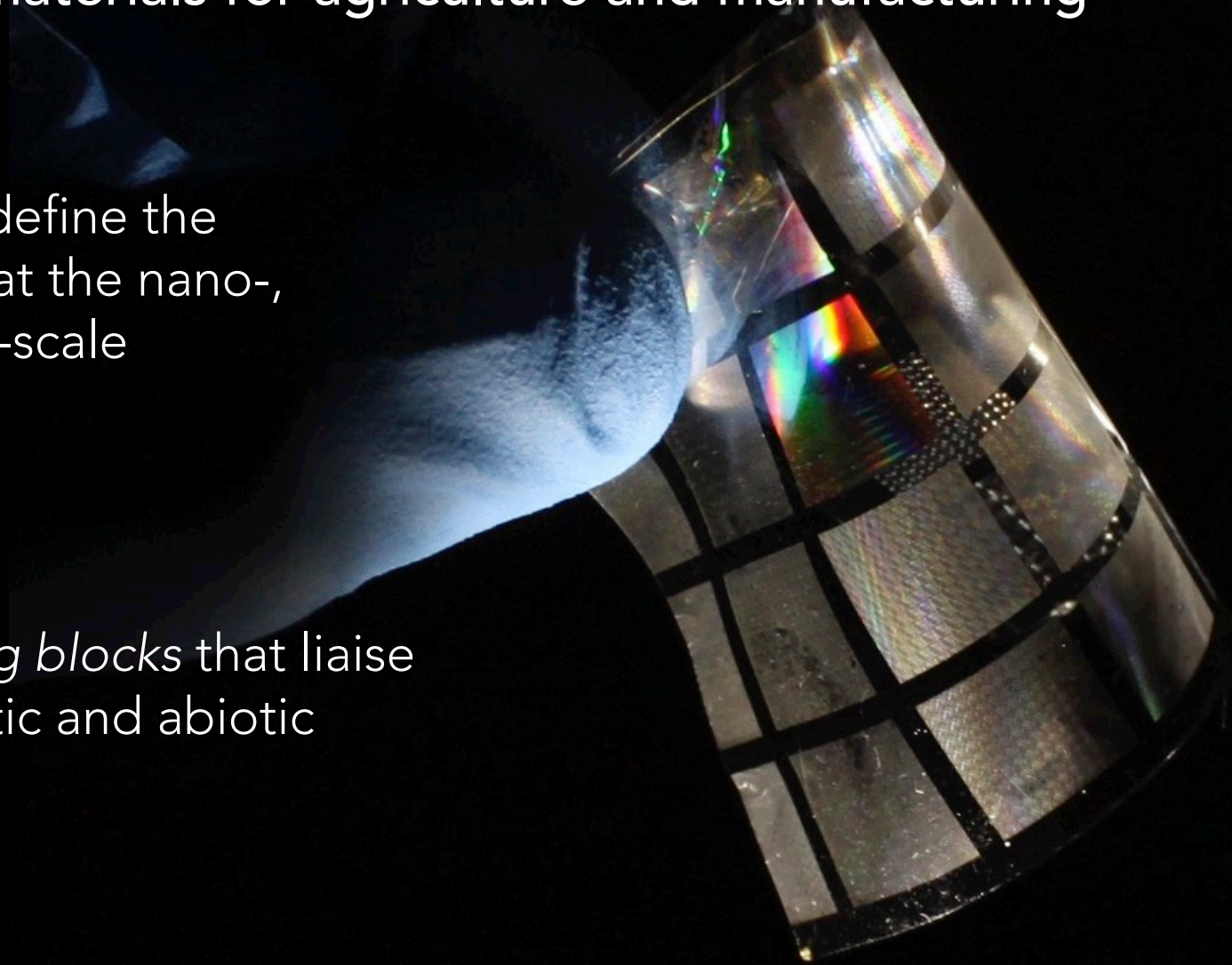
Edible coating for perishable food preservation



Structural biopolymers provide an unprecedented tool to address the technological thirst for innovative solutions in advanced materials for agriculture and manufacturing

New *bricks* to redefine the fabrication rules at the nano-, meso- and micro-scale

Universal *building blocks* that liaise between the biotic and abiotic worlds



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Structural Biopolymers: using Nature's building blocks as an inspiration for advanced manufacturing

Benedetto Marelli, Laboratory for Advanced Biopolymers, CEE @ MIT

Biomaterials tomorrow

- bio-instructive
- respond to their surroundings
- transform themselves
- disappear harmlessly
- biocompatible without sacrificing technological performance
- have "non-obvious" functions

