

Unconventional Hydrogel Scaffolds, Electronics and Machines

Xuanhe Zhao

Soft Active Materials Laboratory

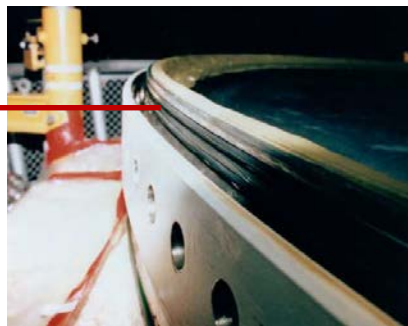
MIT

zhaox.org



2017 MIT Conference
Jan 27 2017

Impact of Soft Materials: from engineering to health



- **Failure of O-ring seal caused the Space Shuttle Challenger disaster in 1986.**
- **Approximately 17 percent of Americans witnessed the launch and disaster.**

Impact of Soft Materials: from engineering to health

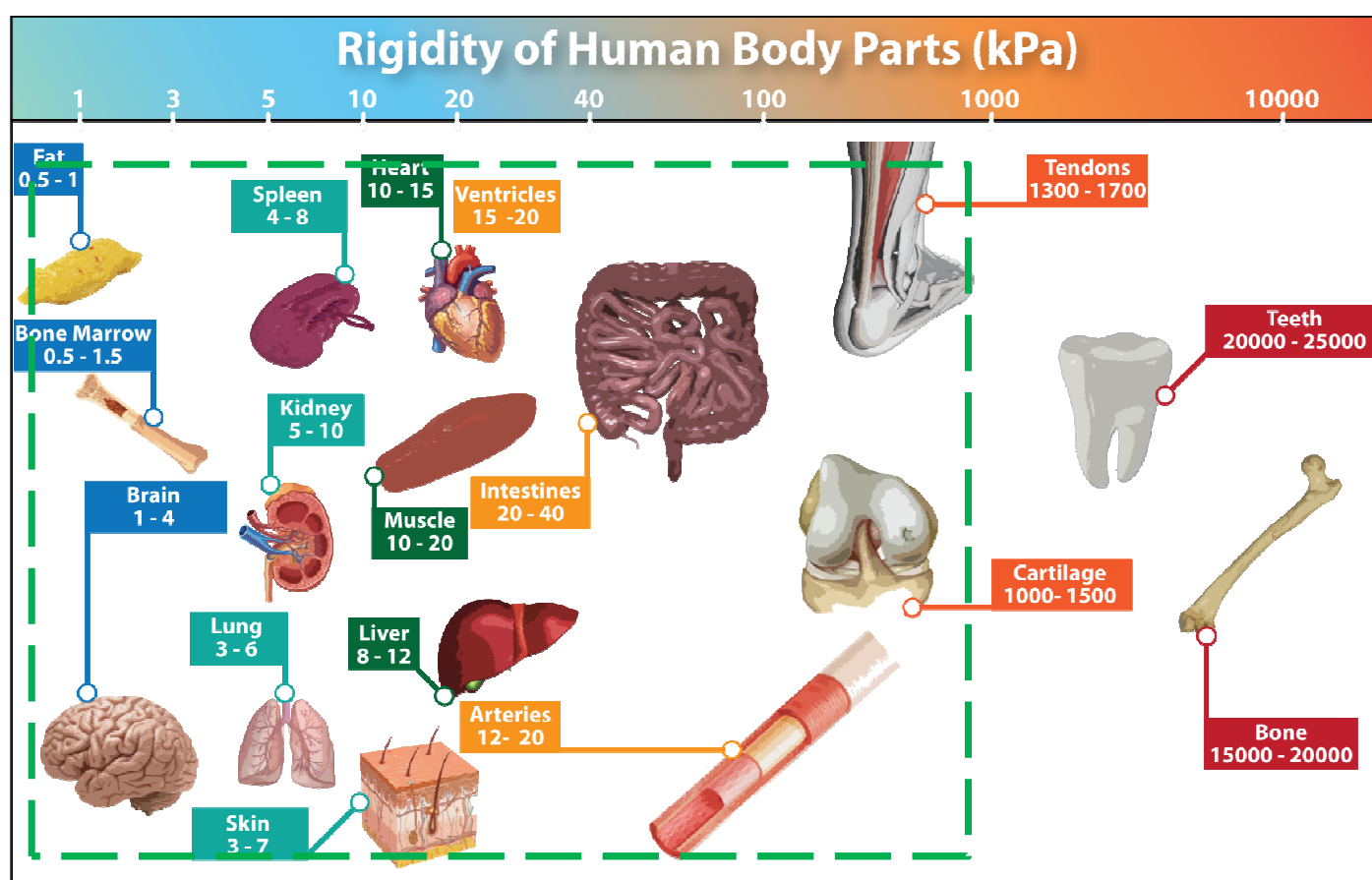


In collaboration
with Samsung
Display



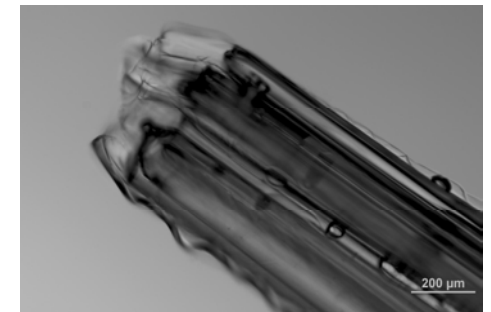
Replace traditional rigid components with polymers and gels to enable flexible electronics and wearable devices.

Impact of Soft Materials: from engineering to health



- **Modulus:** 1kPa~10MPa;
- **Water concentration:** 70%
- **Robust:** under millions of cycles of loads.

Future biomedicine relies on soft materials with similar properties as body.



Hydrogel Neural Probe with Anikeeva

Hydrogels

Extremely Tough

Conventional hydrogels are weak and brittle





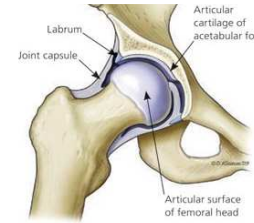
Glass

Conventional hydrogel
Fracture toughness $\sim 1 \text{ Jm}^{-2}$



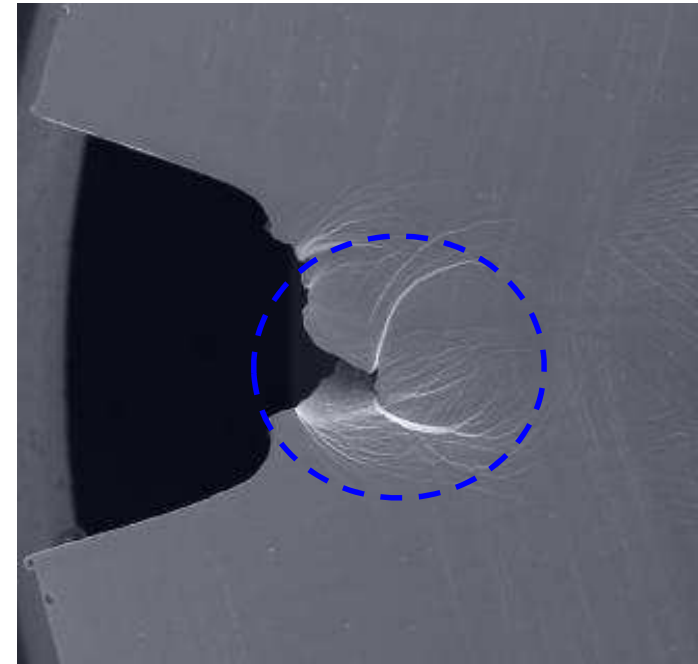
Fracture toughness
= Surface energy

Zhao, Soft Matter, 10, 672 (2014)



Metal

Cartilage
Fracture toughness
 $\sim 1,000 \text{ Jm}^{-2}$



Fracture toughness
= Surface energy +
Dissipation in a zone

1 nm 10 nm 100 nm 1 μm 10 μm 100 μm 1 mm

	Stretchy network						New Mechanism
Mechanical dissipation							
1 nm							
10 nm							
100 nm							
1 μm							
10 μm							
100 μm							
1 mm							
New Mechanism							

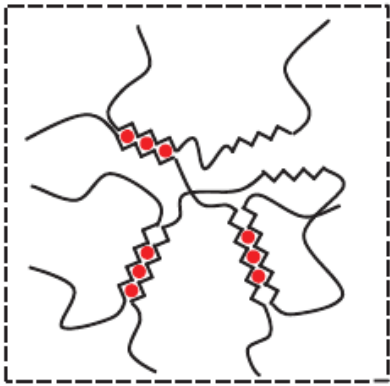
Zhao, *Soft Matter*, **10**, 672 (2014) for previous works

**Build
dissipation
into
stretchy
networks**

Tough hydrogels: build dissipation into stretchy network

Individual Components are very Brittle!

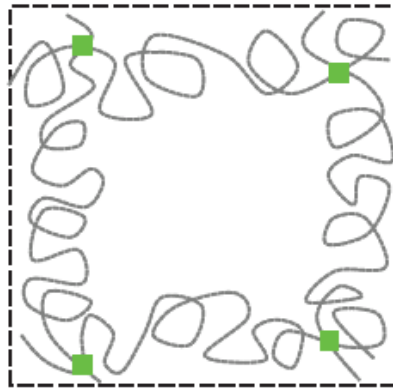
Dissipation



Reversible crosslink:
Alginate Ca^{2+}
dissipates energy



Stretchy network



Long-chain network:
PAAm maintains high
elasticity



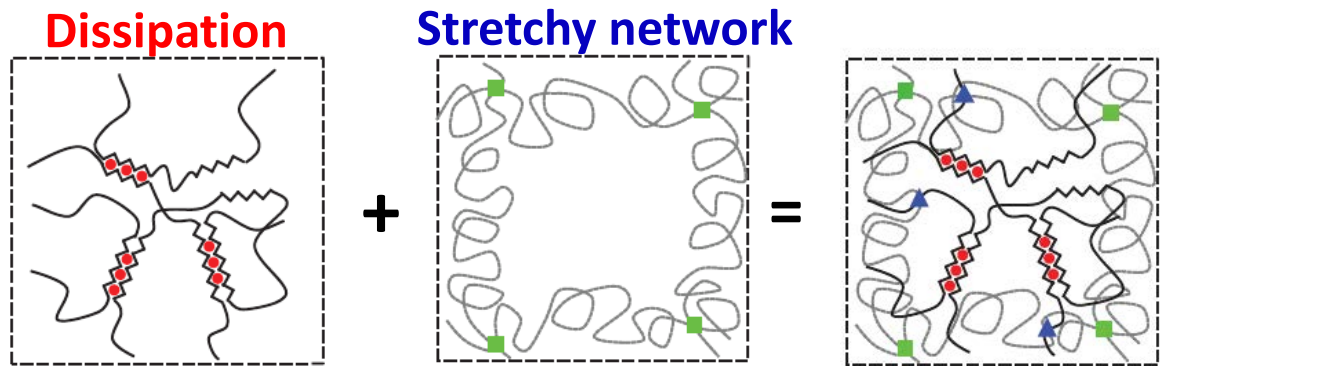
Alginate
 $\sim 50 \text{ Jm}^{-2}$;



PAAm
 $\sim 50 \text{ Jm}^{-2}$

Tough hydrogels: Build dissipation into stretchy network

Nanoscale Interpenetration gives Extremely High Toughness



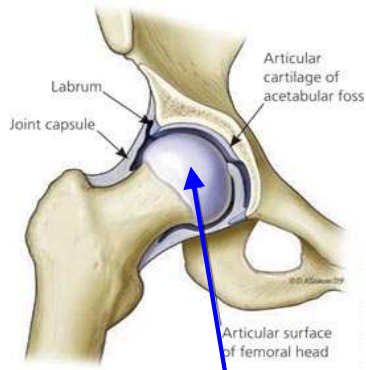
**Reversible crosslink:
Alginate+Ca²⁺**

**Long-chain network:
PAAm**

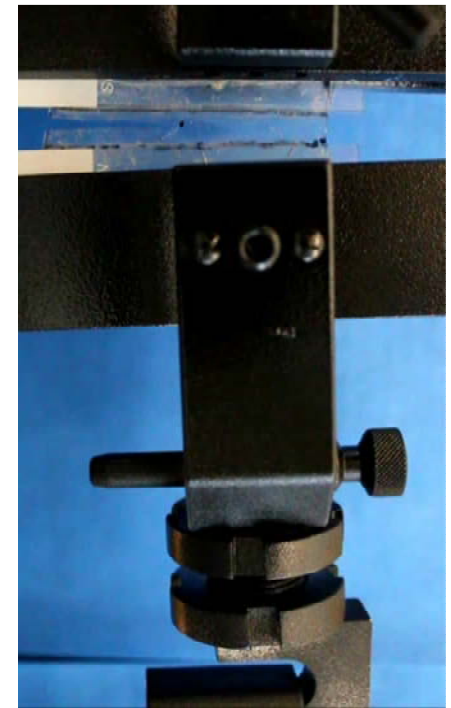
- ~90% water
- Fracture energy 9000 Jm⁻²
- Stretchability 21 times

Sun et al, Nature, **489**, 133 (2012)

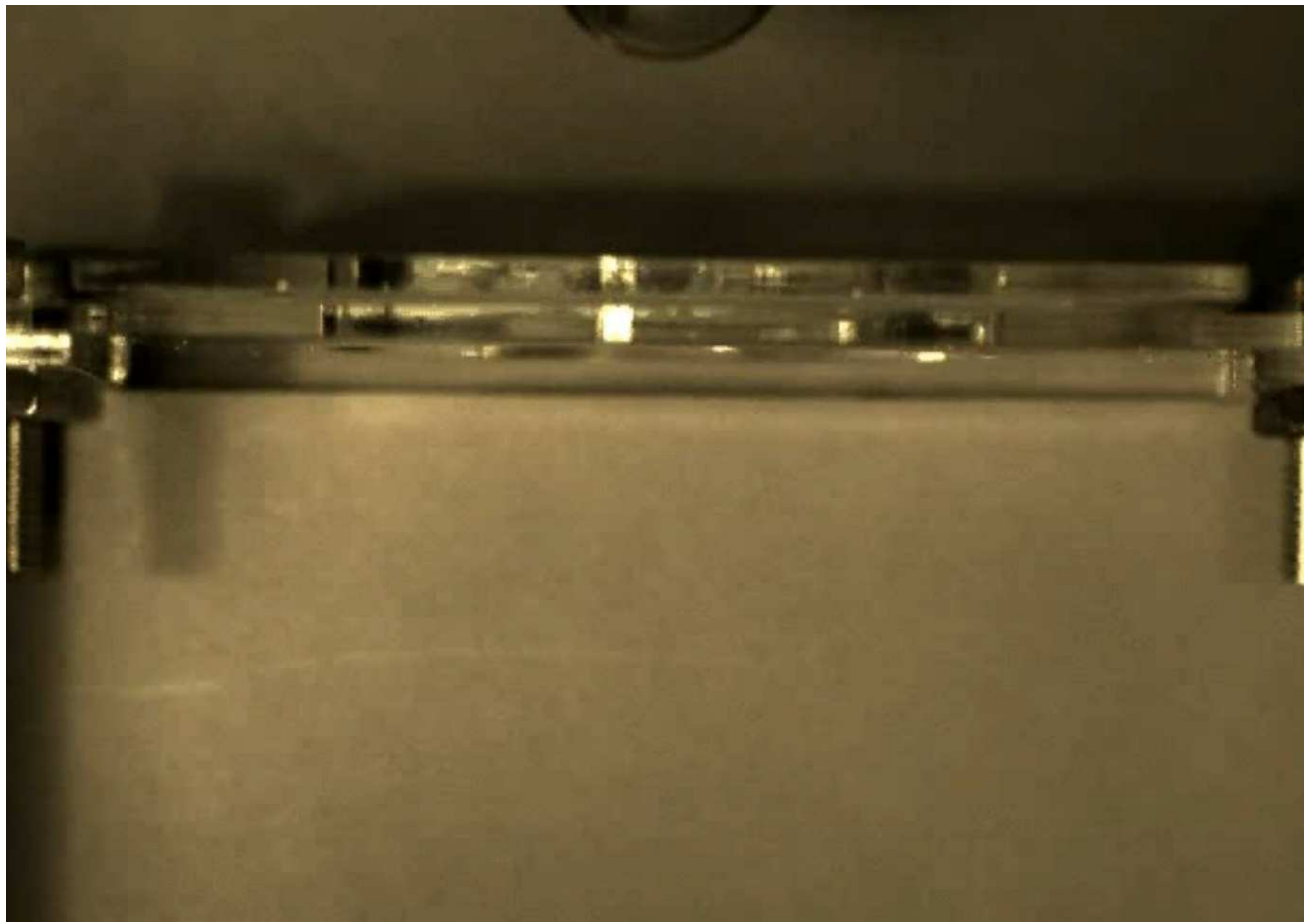
in collaboration with Prof. Suo, Vlassak and Mooney



>1000Jm⁻²



Hydrogel film with 90% water and 1mm thickness



Impact of a ball of 64 g at 6m/s

1 nm 10 nm 100 nm 1 μm 10 μm 100 μm 1 mm

								New Mechanism	
1 nm									
10 nm									
100 nm		▲	▲	▲			▲		
1 μm									
10 μm		▲			▲				
100 μm									
1 mm		▲	Zhao, <i>Soft Matter</i> , 10 , 672 (2014) for previous works					▲	
New Mechanism									

Polymer Candidates:

- PAA
- PAAm
- PEG
- Alginate
- Chitosan
- ELP
-

Nano-filler Candidates:

- CNT
- Graphene
- Graphene oxide
- Nanoclay
-

Macro-fiber Candidates:

- PLG
- PCL
- PGA
-

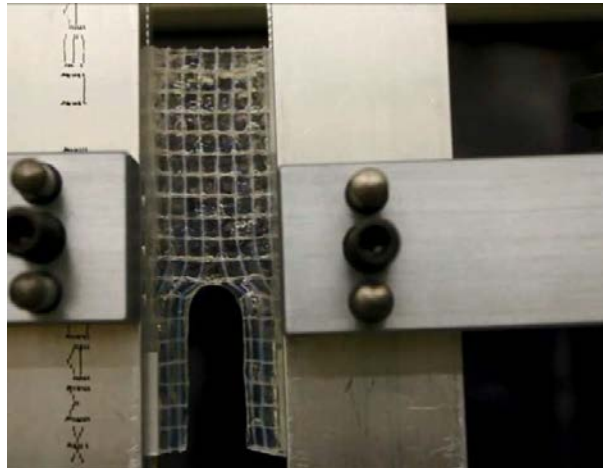
Tough Hydrogels -- A Wide Range of Rigidity with Diverse Polymers



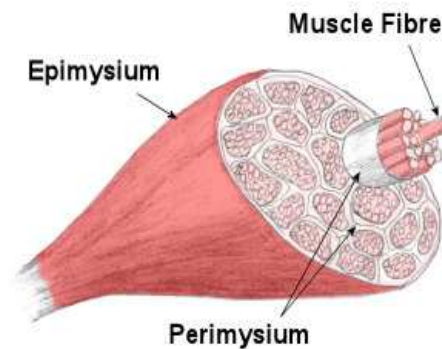
1~5 kPa;
1,000 Jm⁻²



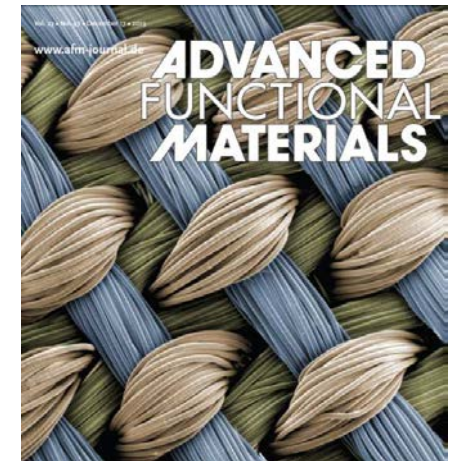
Lin et al, Extreme Mechanics Letters, 1, 70 (2014)



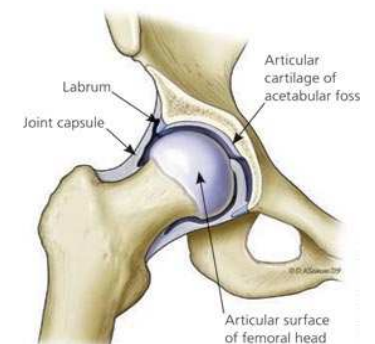
10~100 kPa;
1~10 kJm⁻²



Sun et al, Nature, 489, 133 (2012)
Lin et al Soft Matter, 10, 7519, (2014)

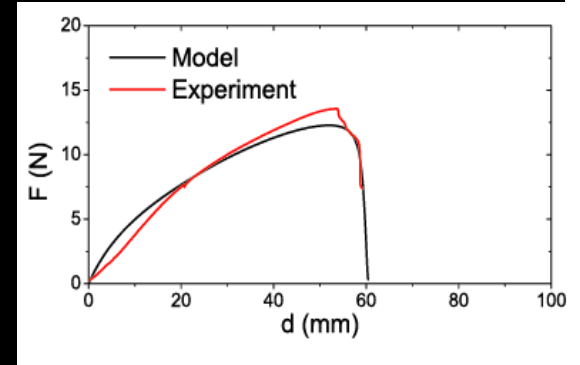
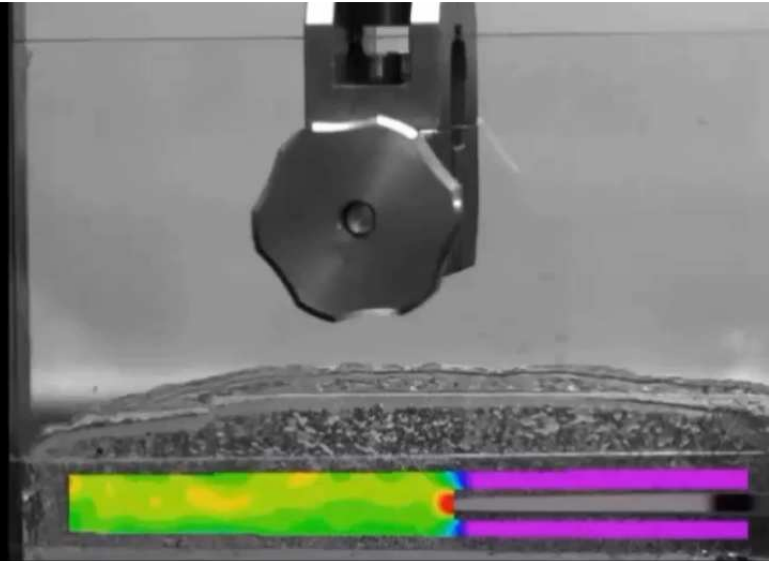


1~10 MPa
10~50 kJm⁻²

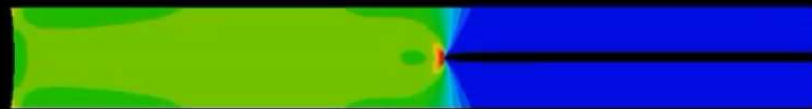


Liao et al, Advanced Functional Materials, 47, 5833 (2013);

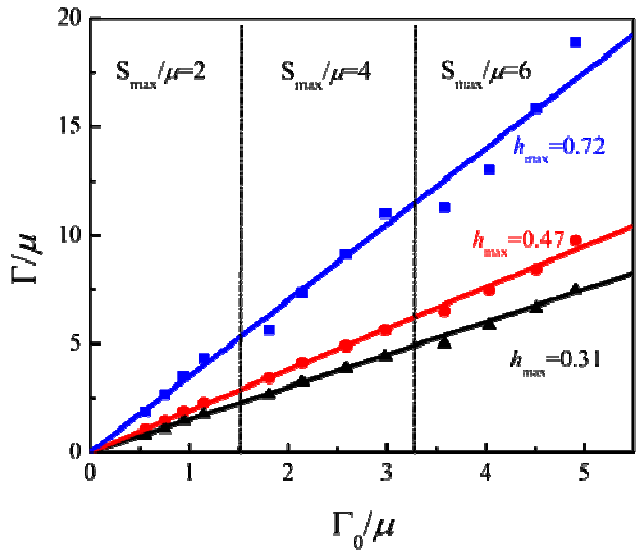
Experiment



Model
(No fitting
parameter)

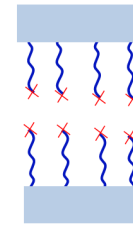


Governing Equation for fracture toughness



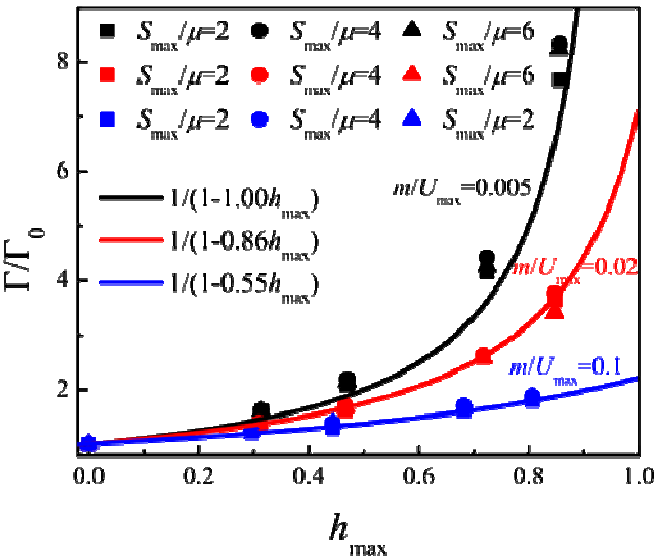
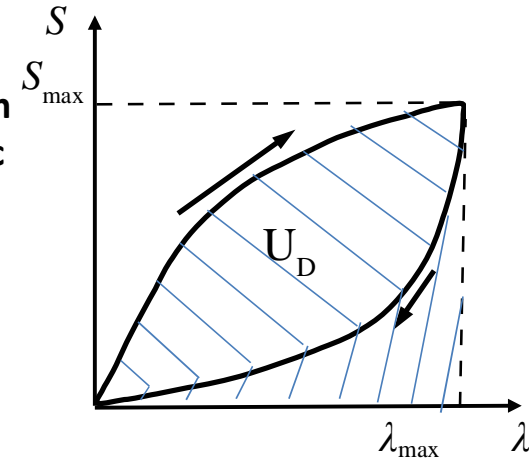
$$\Gamma = \frac{\Gamma_0}{1 - \alpha \cdot h_{\max}}$$

Intrinsic Fracture Energy



Maximum hysteretic ratio

$\alpha \approx 1$ for stretchy materials

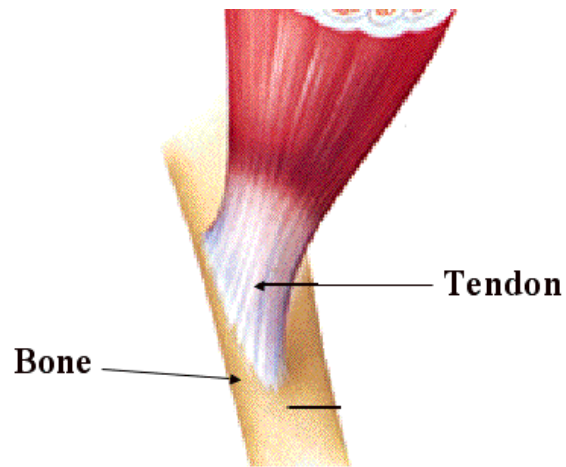
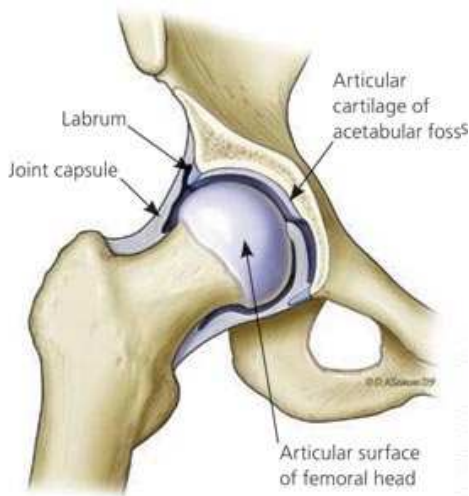


Zhang et al, EML, 4, 1 (2015)

Hydrogels

Extremely Adhesive

Adhesive Hydrogels in Nature

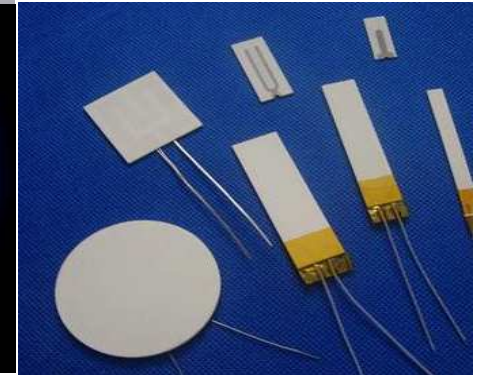
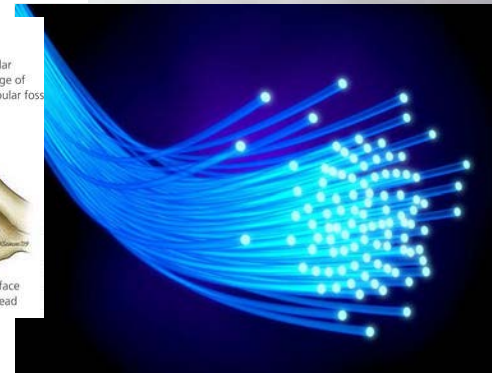
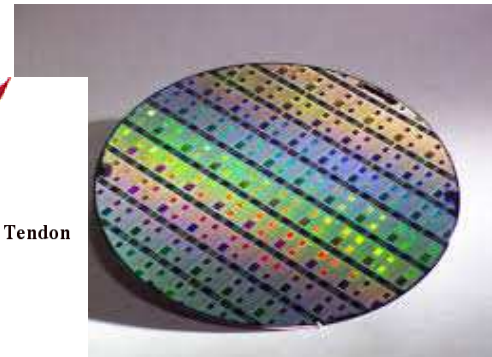
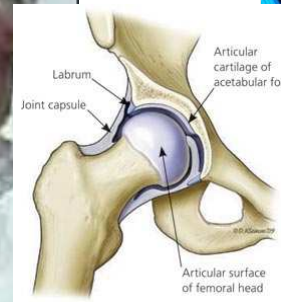
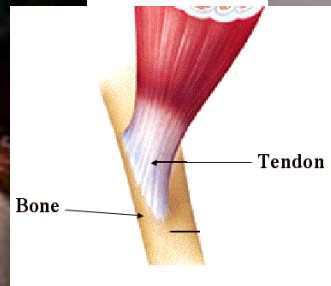


Interfacial toughness $\sim 800\text{Jm}^{-2}$

Design Adhesive Hydrogels



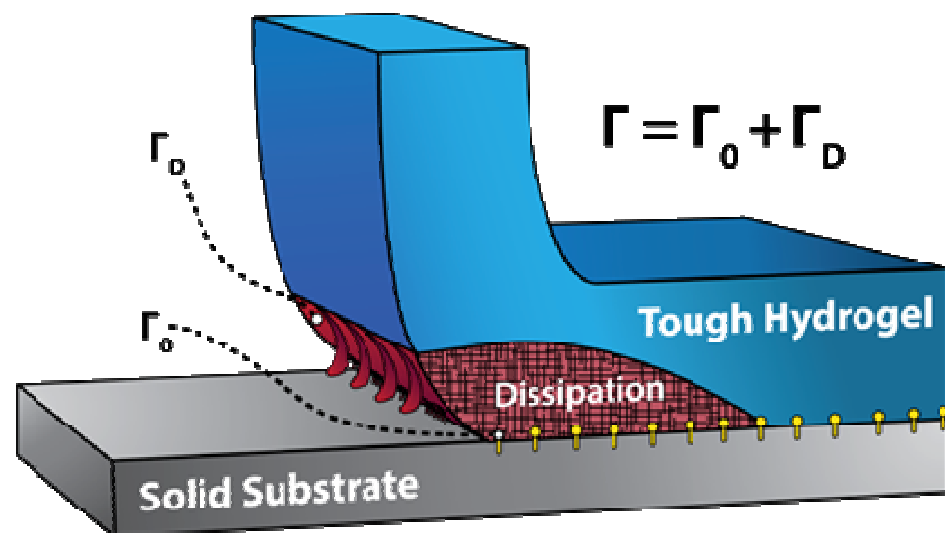
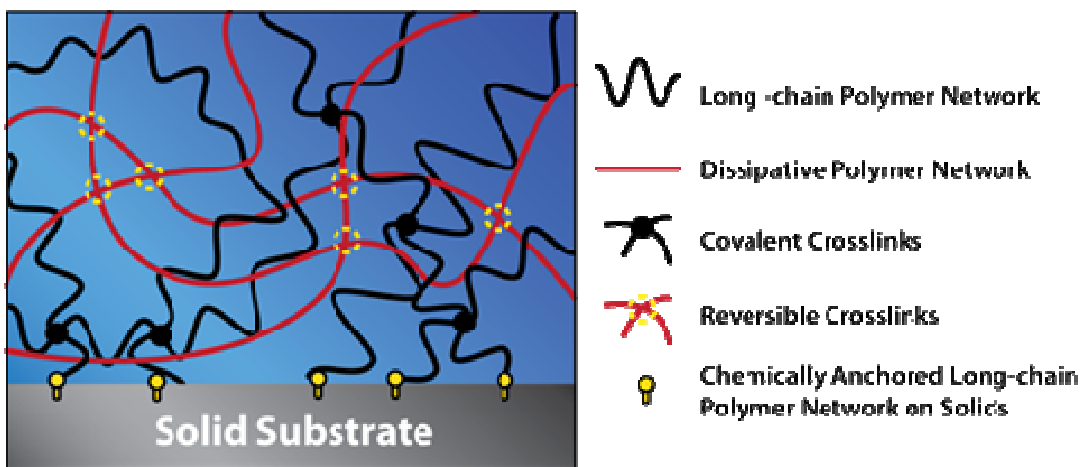
90% water; ~kPa



Diverse engineering solids; MPa~GPa

Tough Hydrogels: Build dissipation into stretchy network.

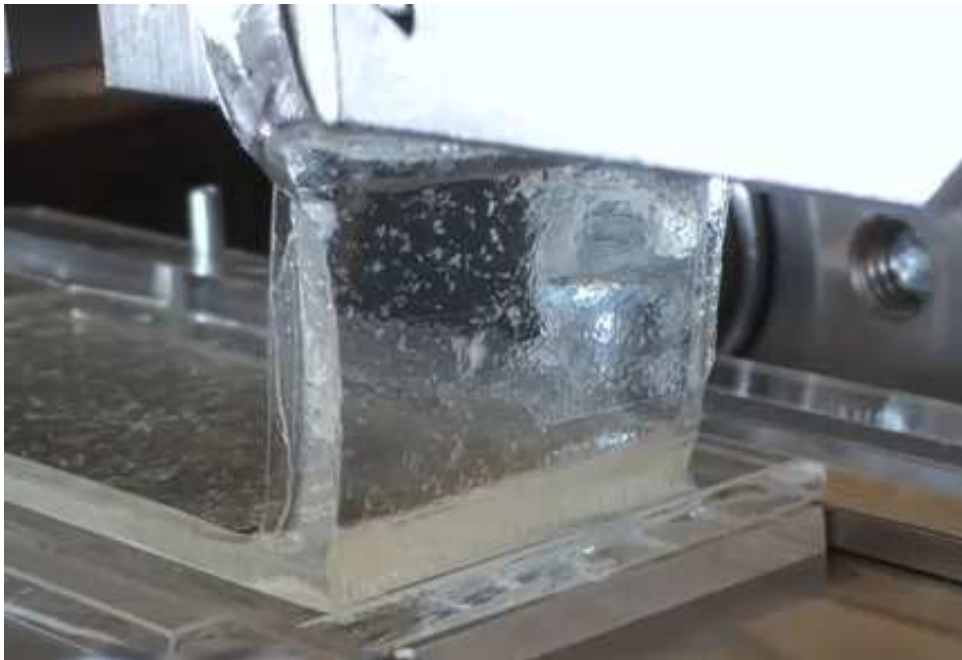
Adhesive Hydrogels: Anchor stretchy network on hard material.



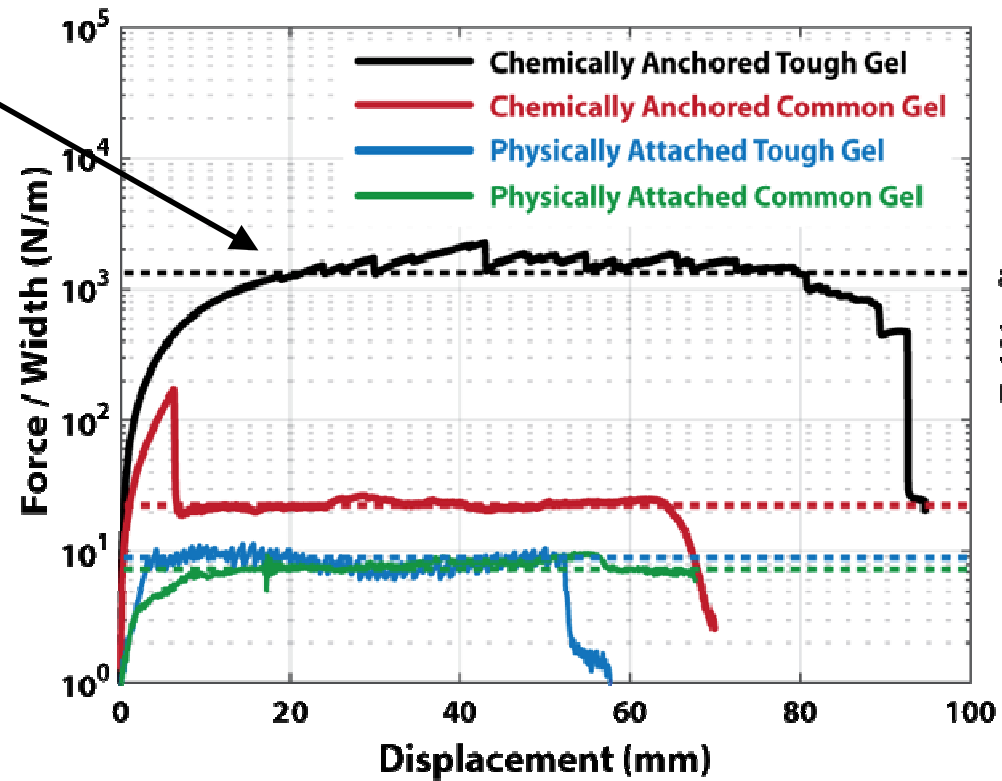
Yuk et al, Nature Materials, 15, 190-196 (2016);

Yuk et al, Nature Communications, 7, 12028 (2016)

Hydrogels with 90% water bonded on Si, SiO₂, glass, ceramics, Ti, Al, Fe et al

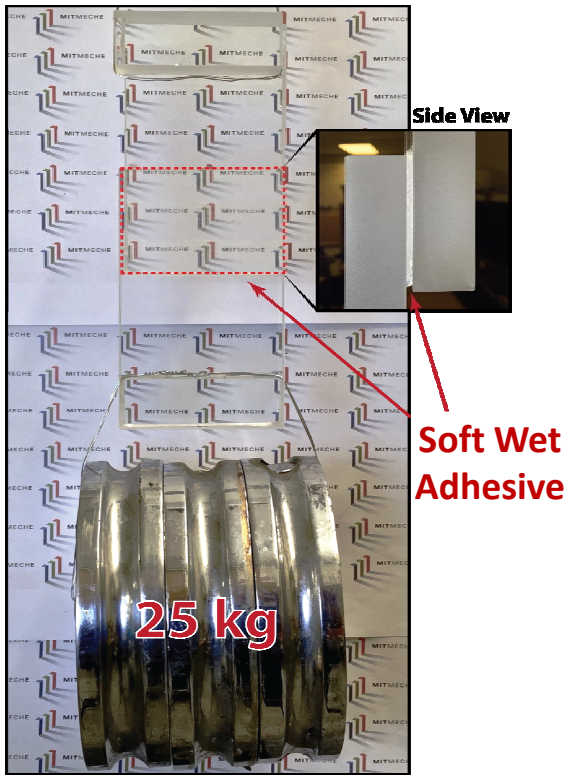


Detachment and Finger Instability



Yuk et al, Nature Materials, 15, 190-196 (2016);

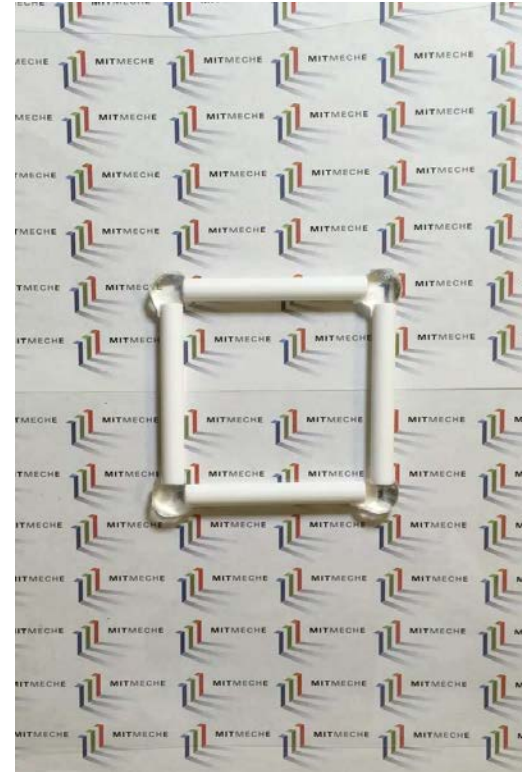
Hydrogel-Engineering Material Hybrids



With glass

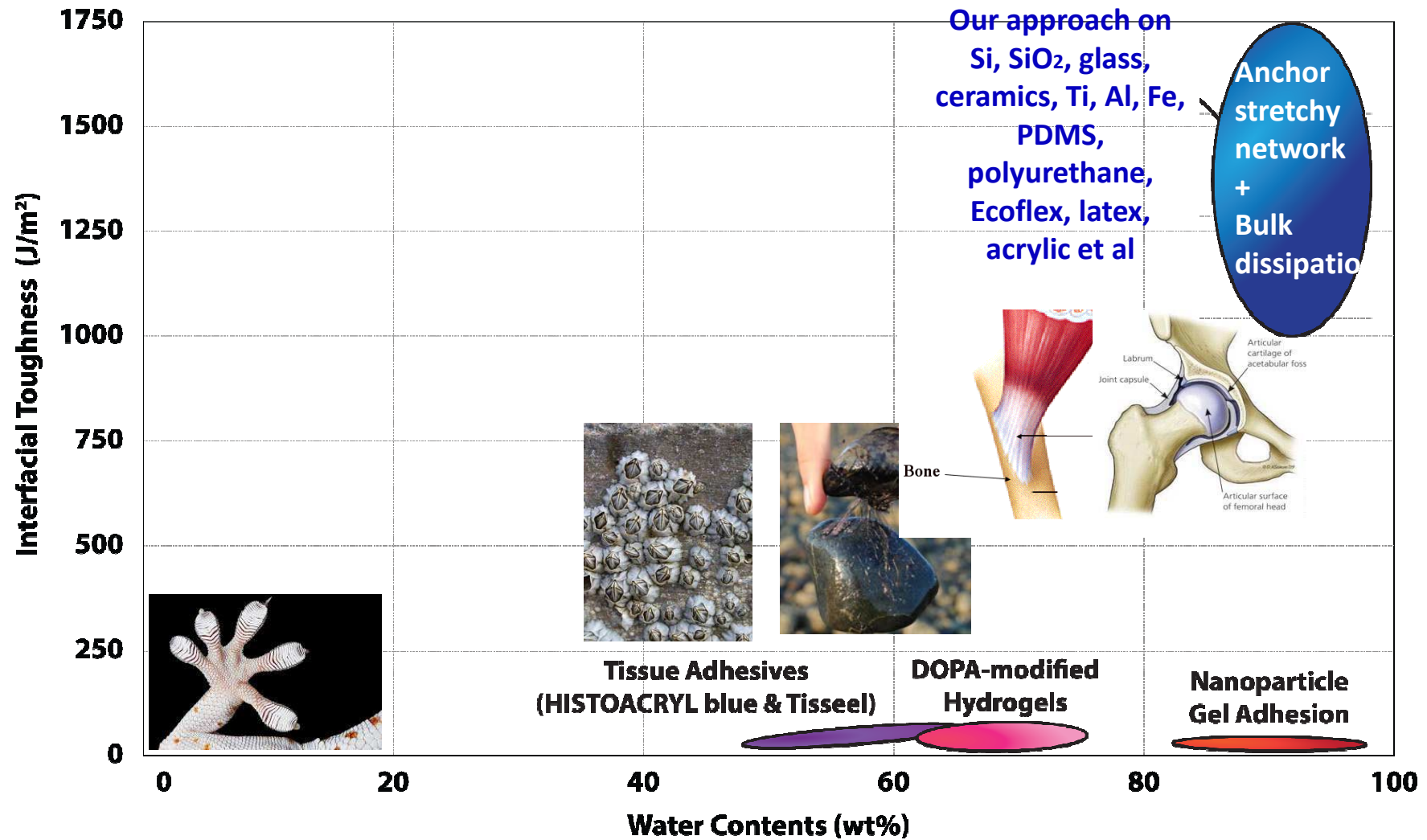


With silicon

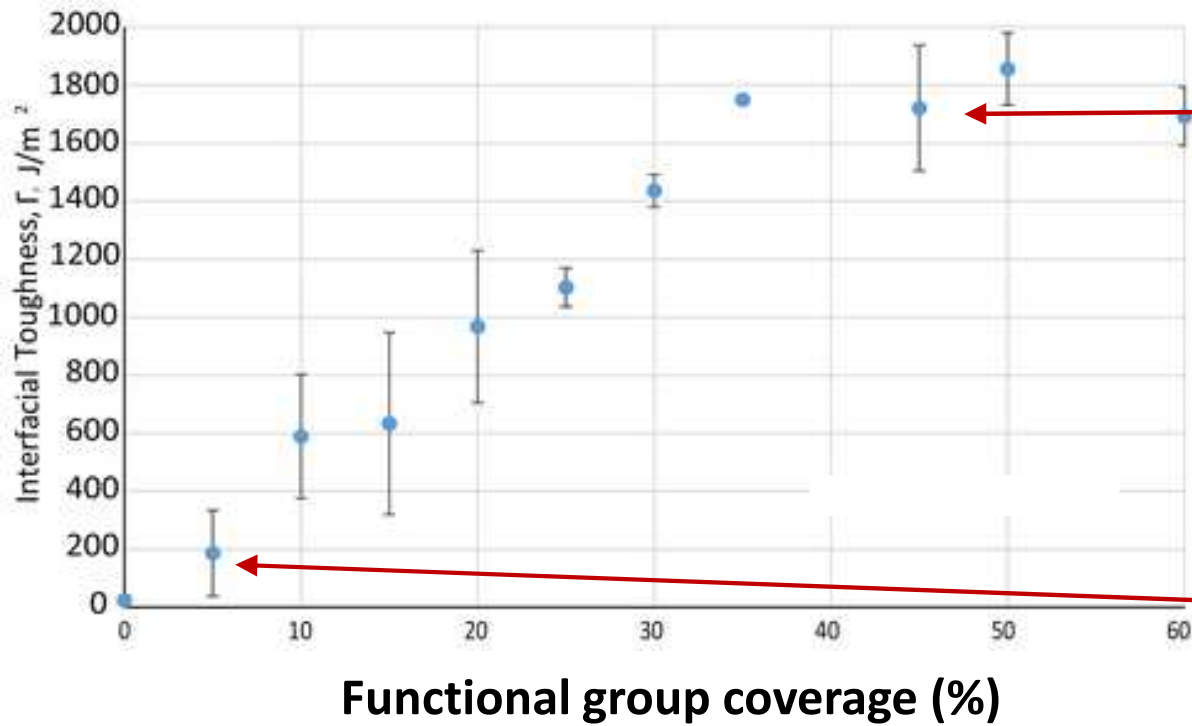


With ceramics





Tunable Adhesion from 1 to 1000 Jm⁻²

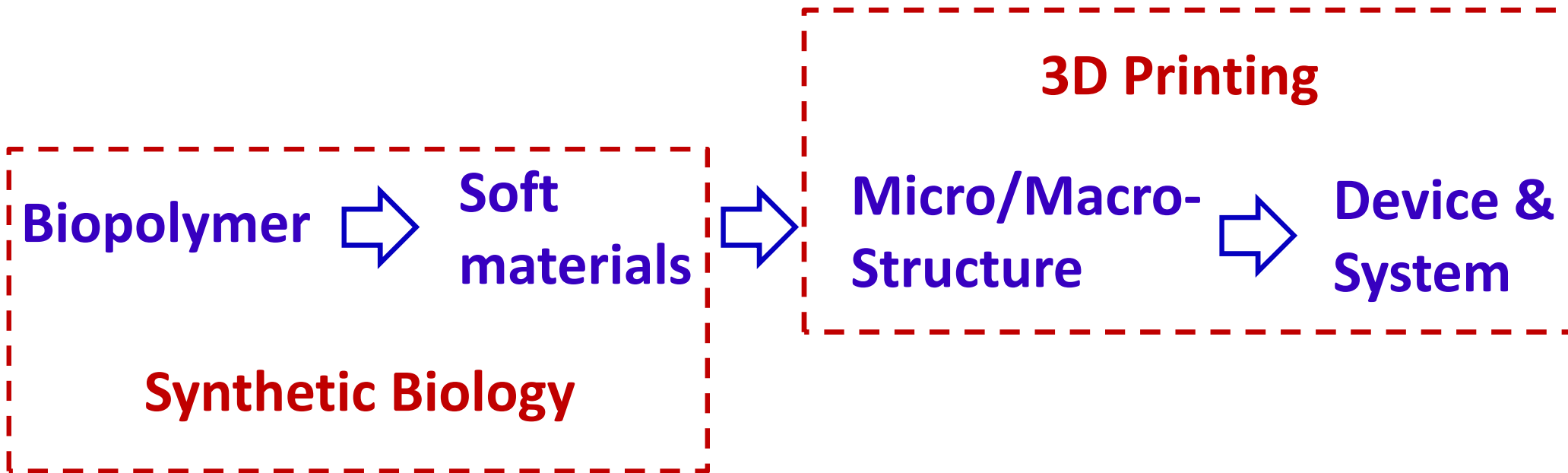


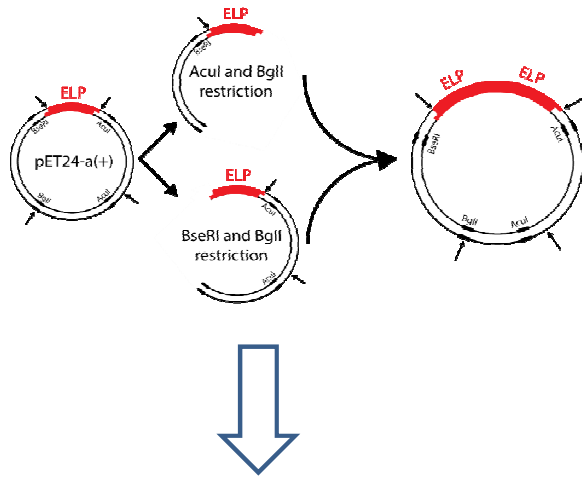
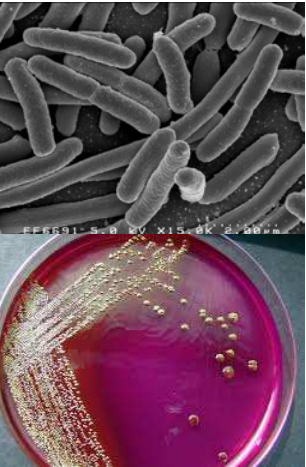
Parada et al, In submission (2017)



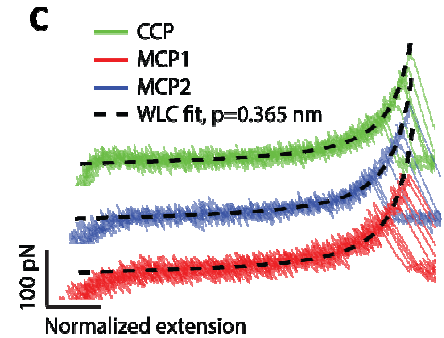
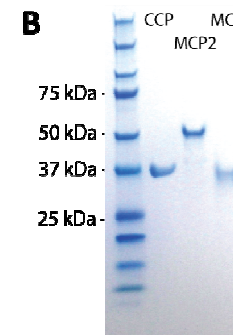
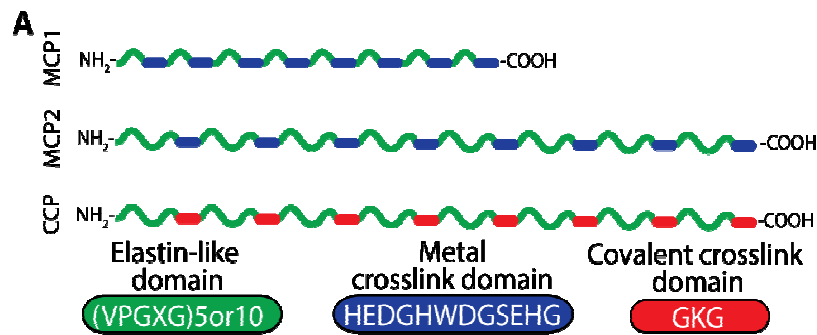
Hydrogels

Manufacturing





Biopolymers Designed by Synthetic Biology

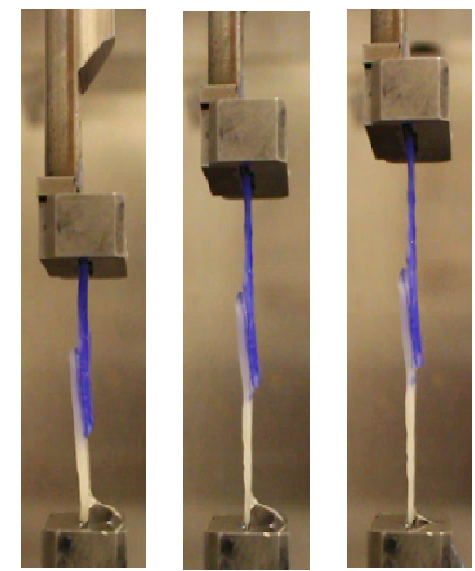
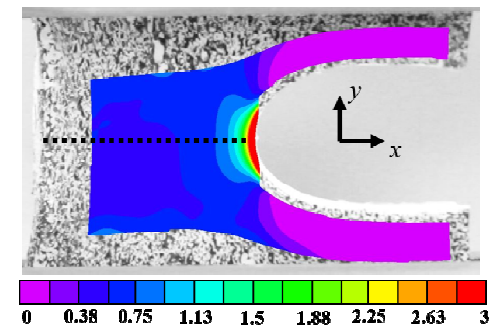
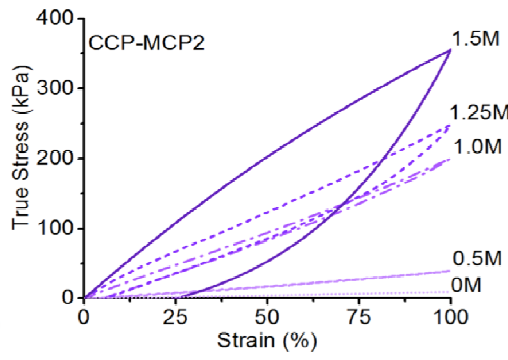
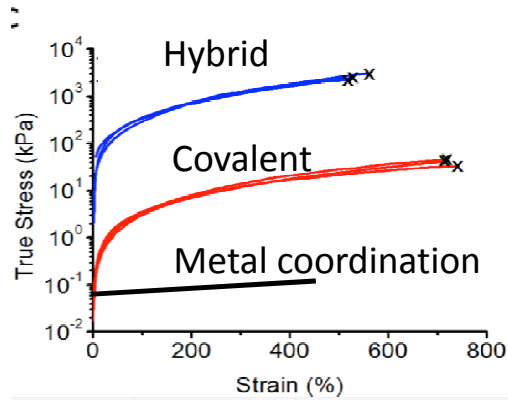


Ghoorchian et al
Adv. Funct. Mater.,
 DOI:10.1002/adfm.
 201500699 (2015)

Gonzalez et al,
 Unpublished (2015)

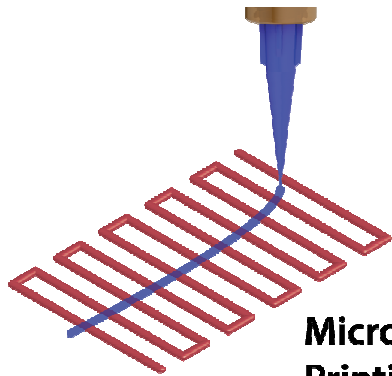
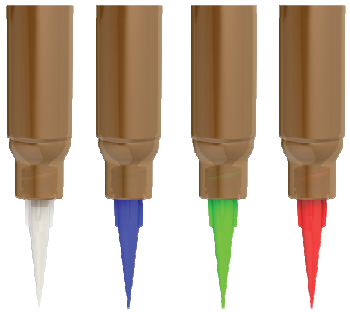
In collaboration with Gabriel Lopez and Tosh Chilkoti at Duke

Biopolymers Designed by Synthetic Biology

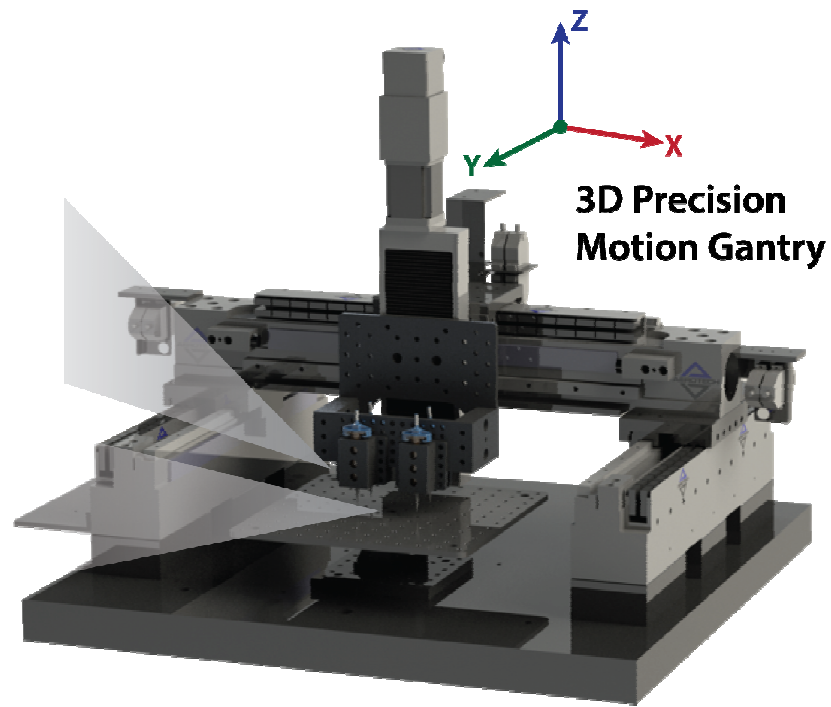


Multi-material 3D Bio-printer

Multi-material inks

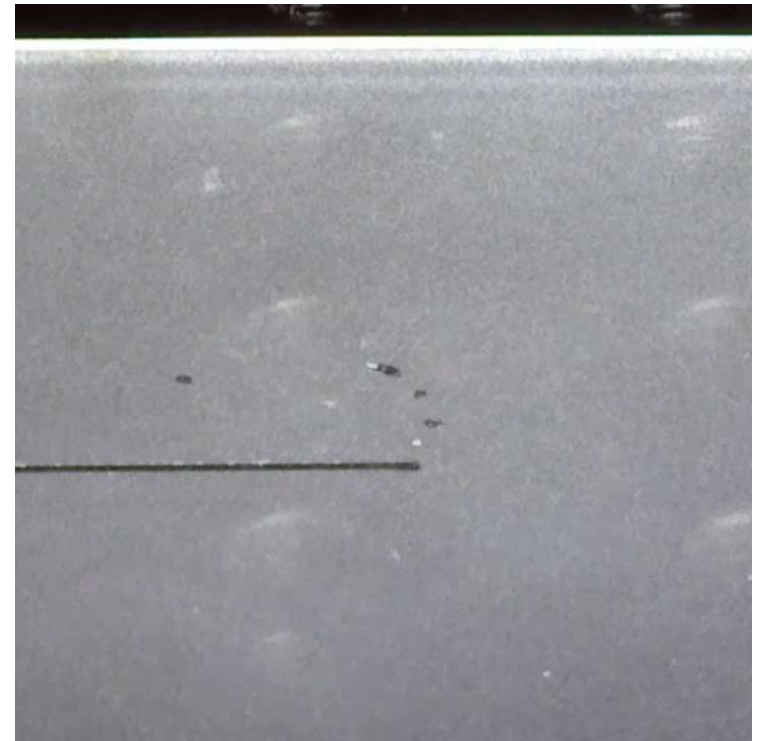
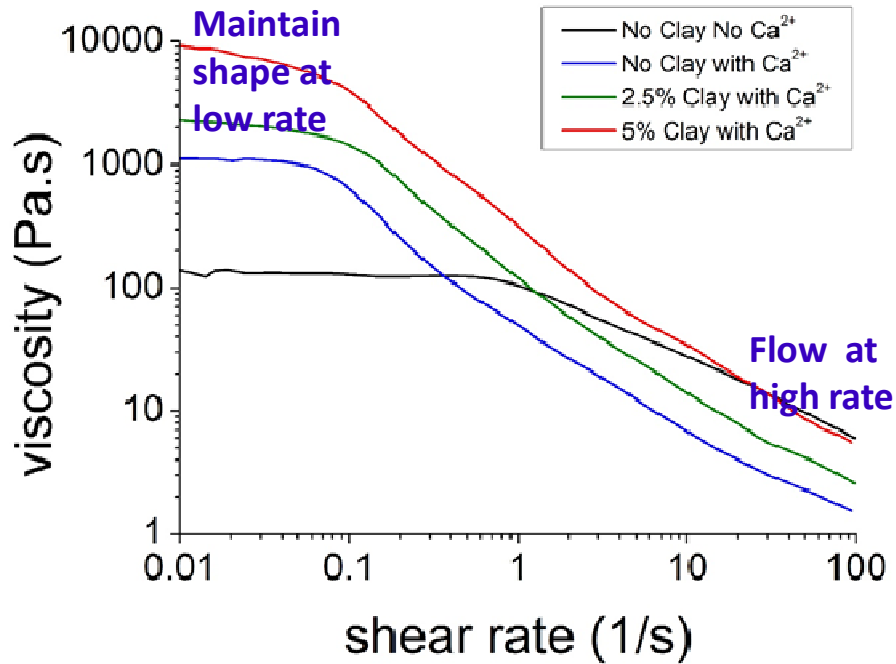


Microscale
Printing of Diverse Materials



- Micro-extrusion based
- Resolution up to **5um.**
- Printing **multiple** materials in one structure
- Particularly suitable for **soft materials and biomaterials.**

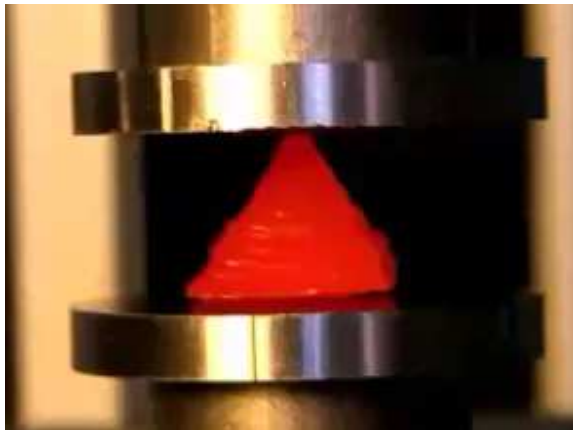
Microstructures Manufactured by 3D Printing



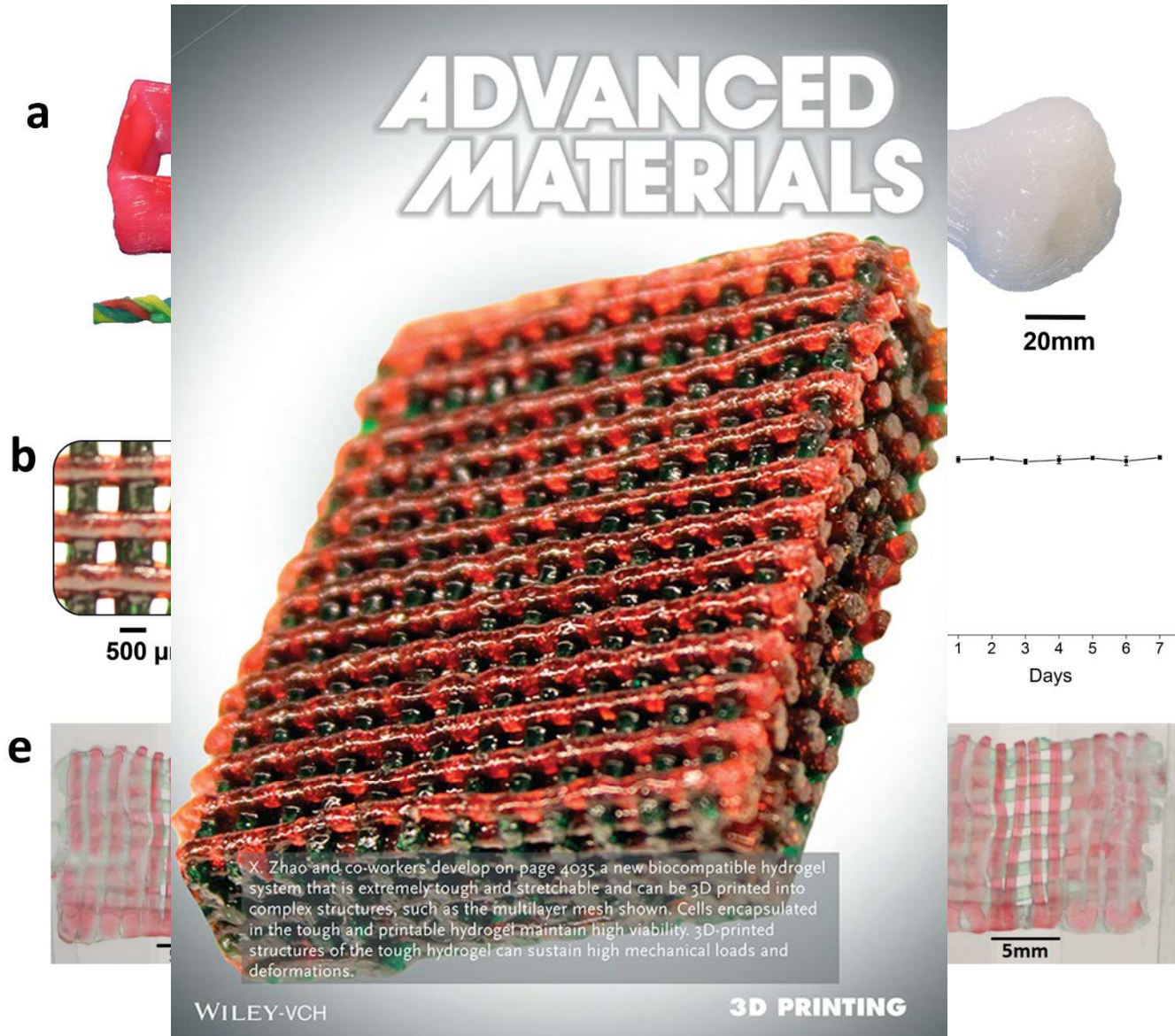
Ink: Shear-thinned polymer solution & Unconventional networks

Hong et al Advance Materials, 27, 4035 (2015)

Tough Soft Microstructures by 3D Printing



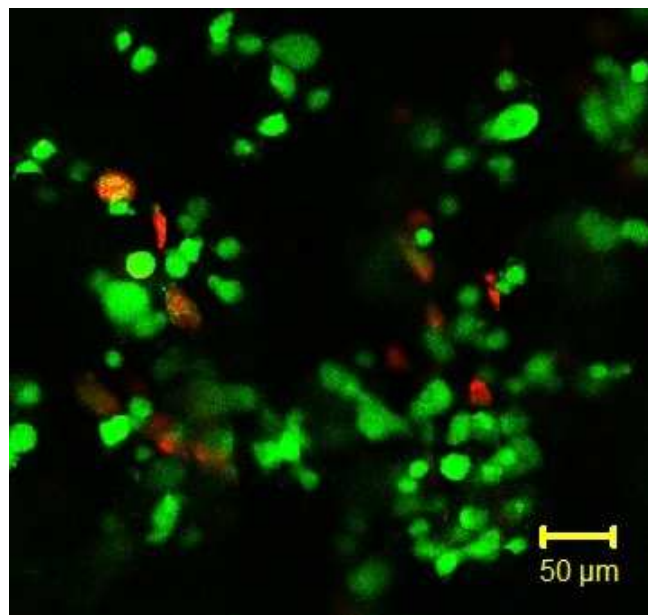
Hong et al Advance
Materials, 27, 4035 (2015)



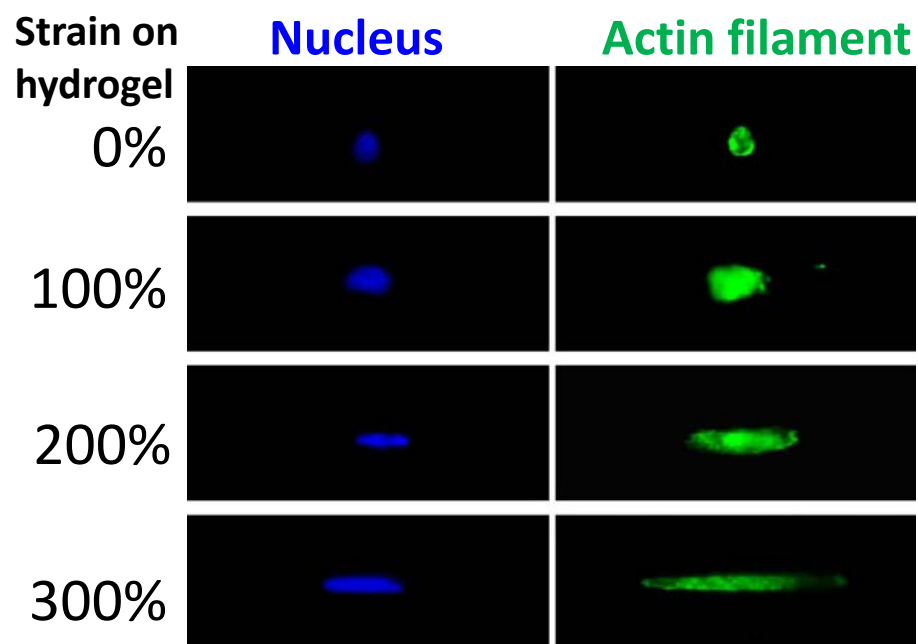
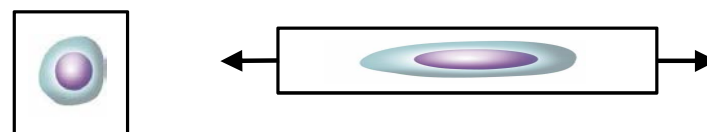
Hydrogels

Bio-scaffolds, Electronics, Machines and Robots

Growing Cells and Tissues in Hydrogel Scaffolds

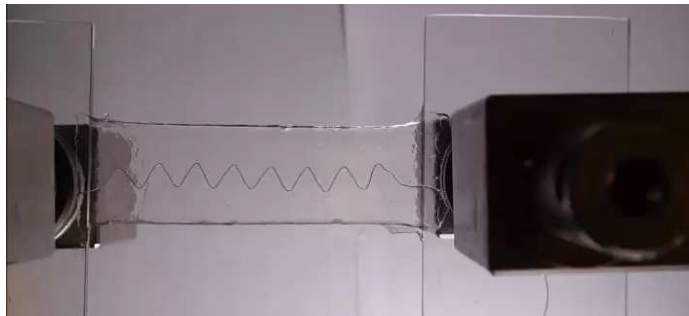


Human mesenchymal stem cells (hMSC)
live dead assay

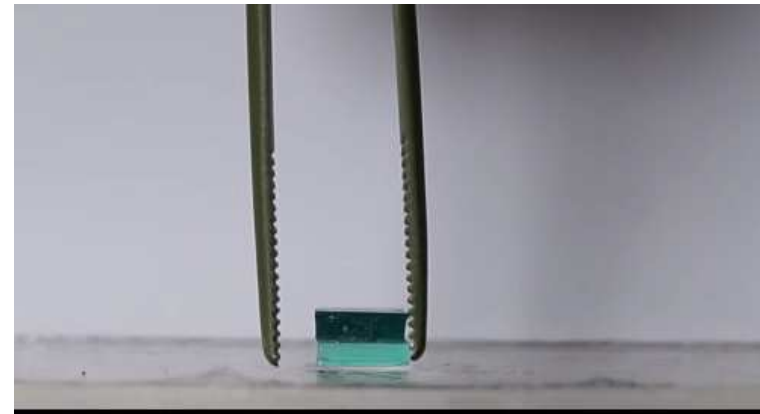


Hong et al Advance Materials, 27, 4035 (2015)

Integrating Electronics with hydrogels (70~90% water)



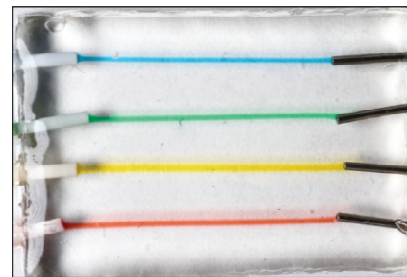
Conductive wires



Functional islands



LED arrays



t = 0 min, $\lambda = 1$

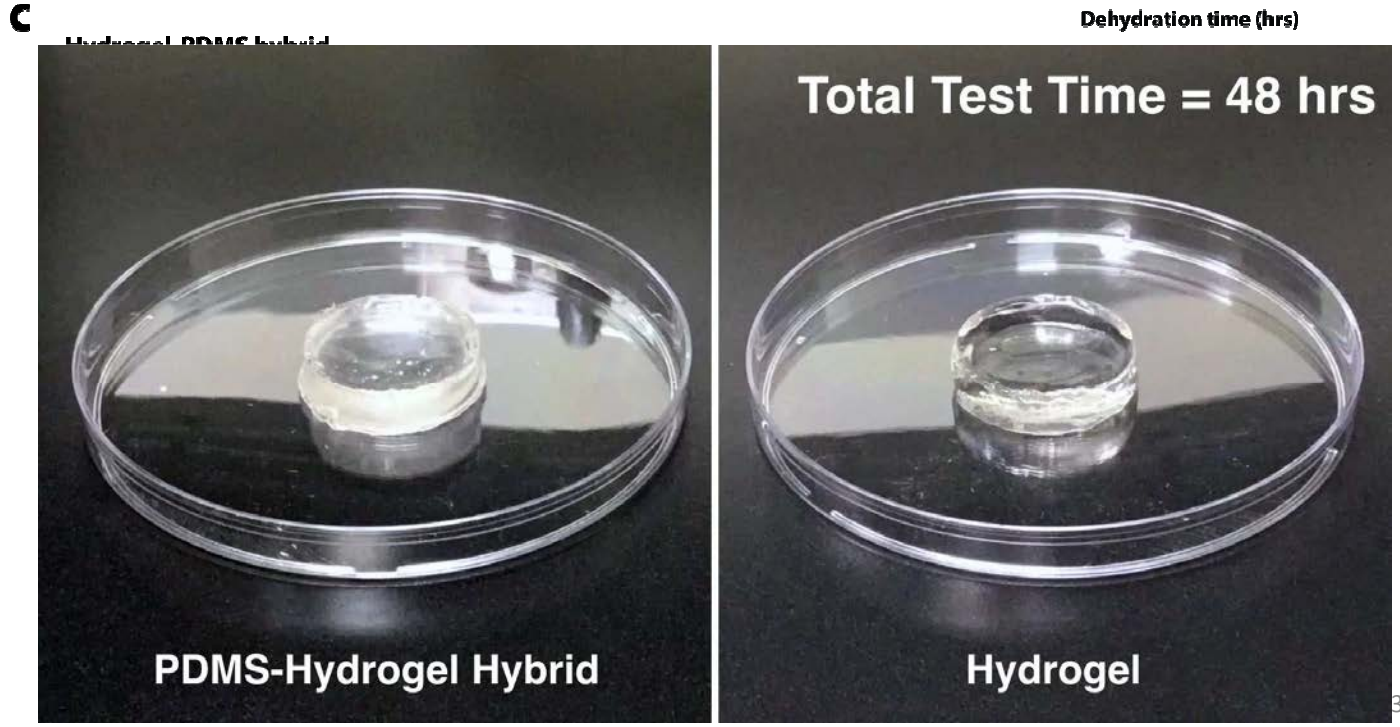
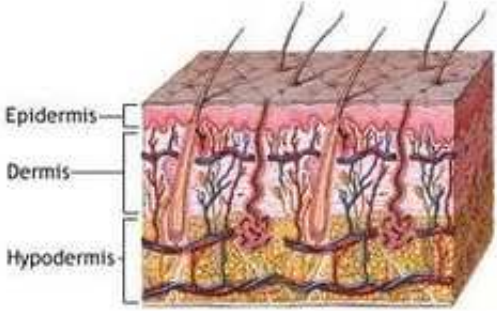
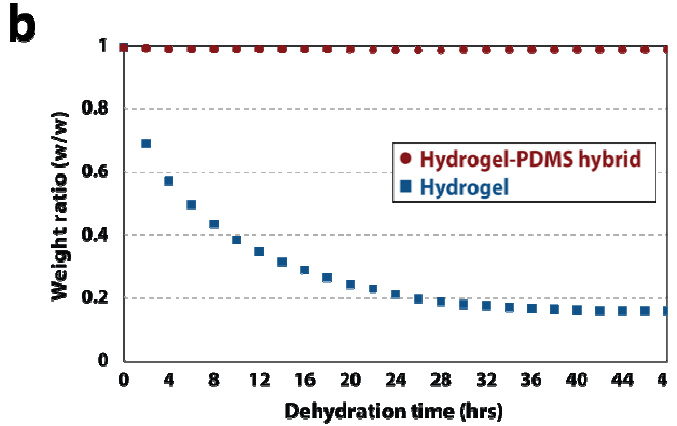
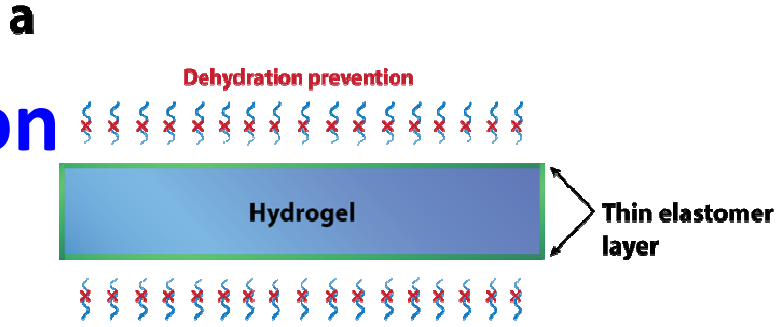


t = 120 min, $\lambda = 1$

Drug delivery channels

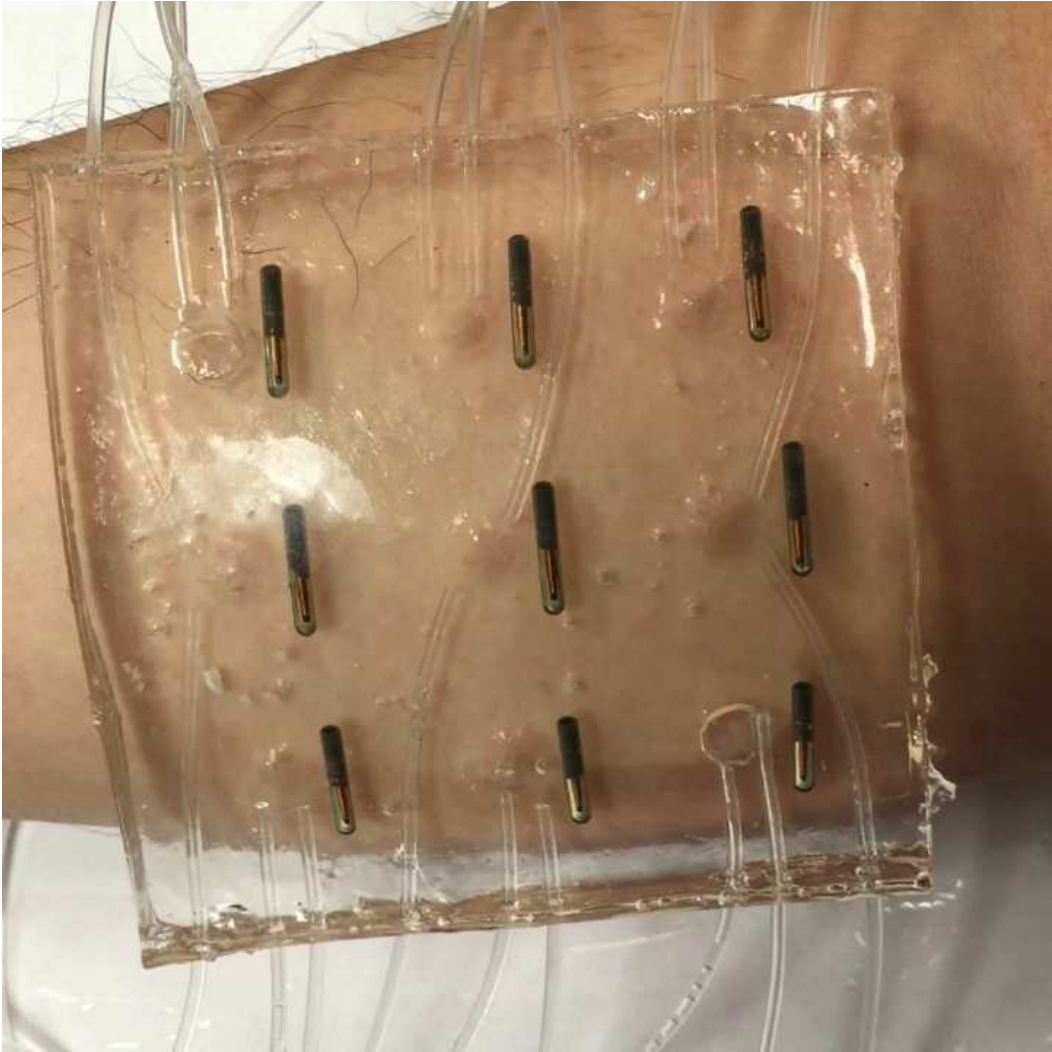
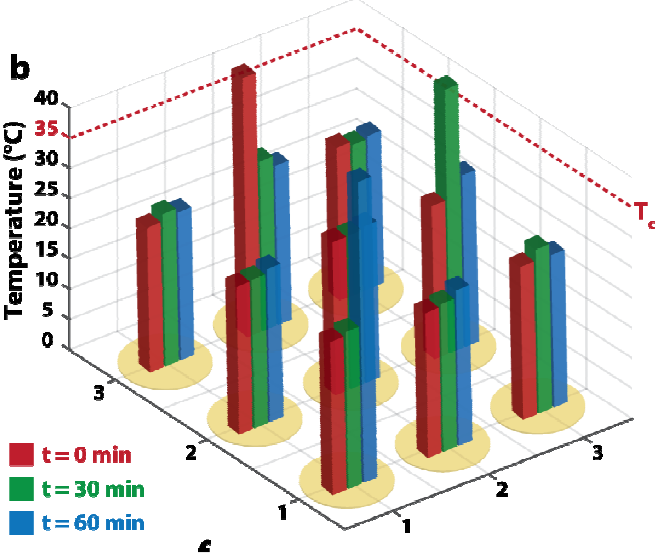
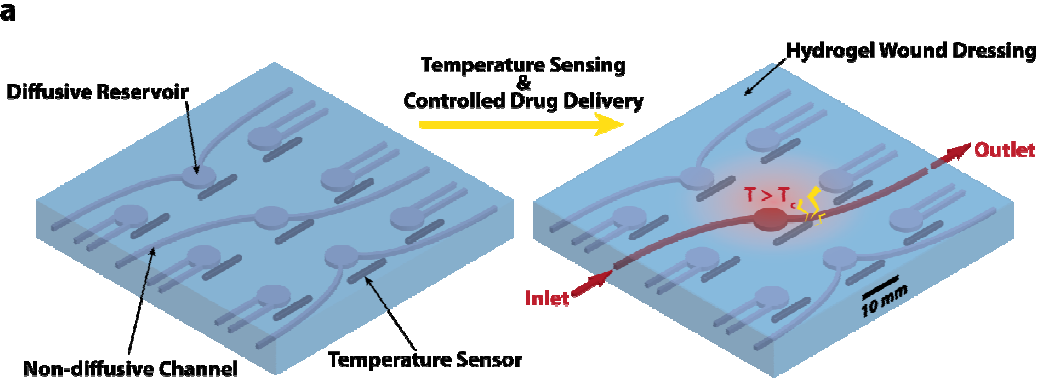
Lin, et al, Advanced Materials, 28, 4497–4505(2016)

Anti-dehydration hydrogel



Yuk et al, Nature Communications, In press (2016)

Smart Hydrogel Band-Aid

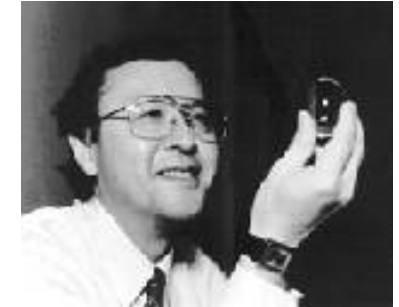
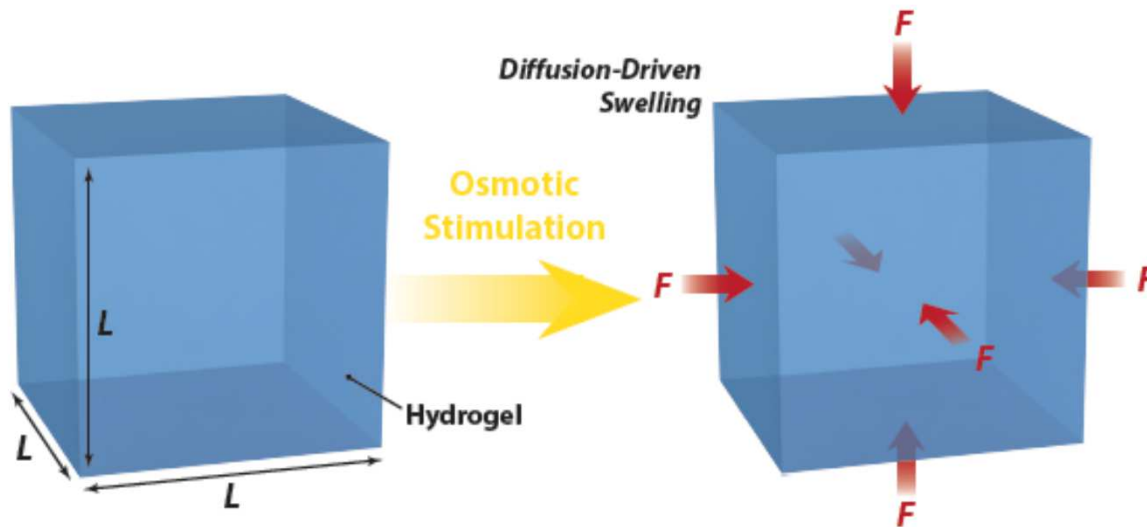


Lin, et al, *Advanced Materials*, 28, 4497–4505(2016)

Hydrogel Robots



Existing Hydrogel Actuators are Mostly Osmotic-Driven



Toyoichi Tanaka (1946-2000)
Professor of Physics, MIT

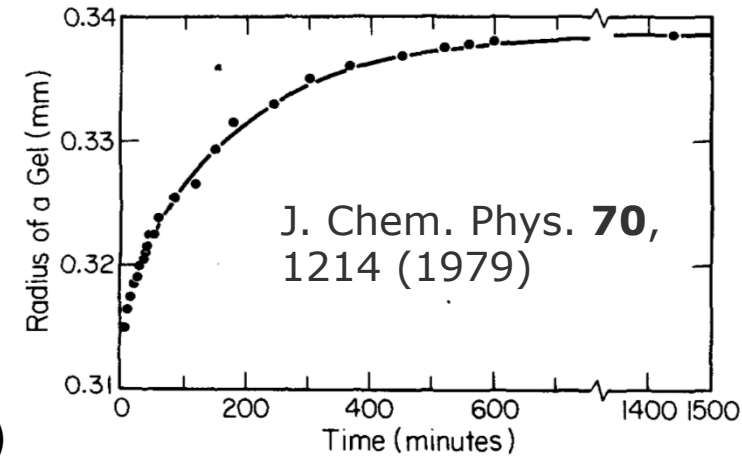
$$F \propto \Delta\Pi L^2 \sim 10N$$

$$t \propto L^2 / D \sim 10^6 s$$

$$\Delta\Pi \sim 100kPa$$

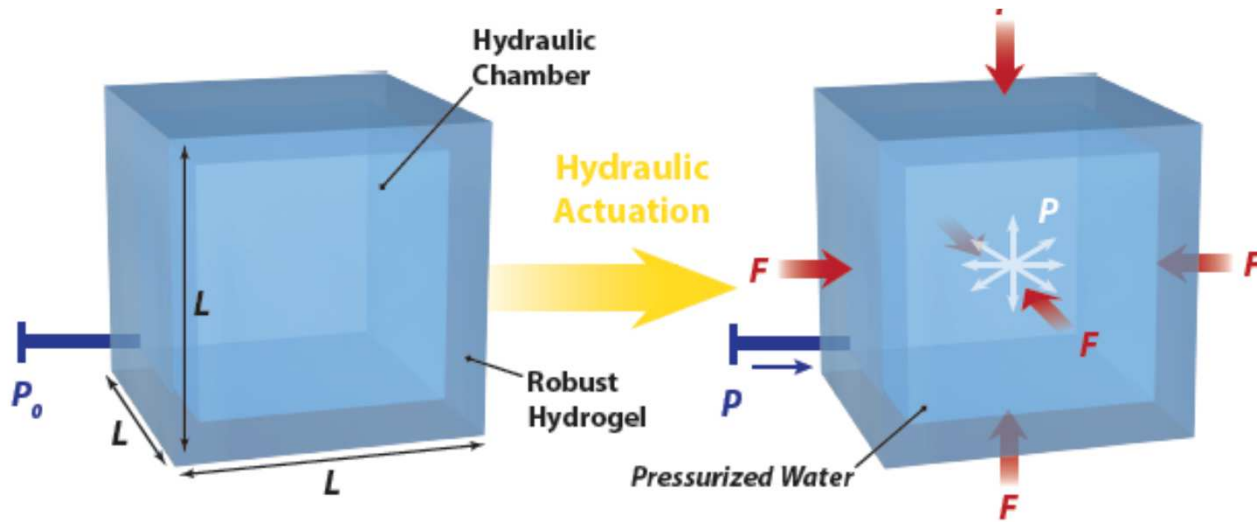
$$L \sim cm$$

$$D \sim 10^{-10} m^2 / s$$



Zhao et al, PNAS, **108**, 67 (2011); Hong et al, JMPS **58**, 558-577 (2010)

Hydraulic Actuation of Tough Hydrogel Structures



$$F \propto \Delta P L^2 \sim 10N$$

$$t = t_{external} < 1s$$

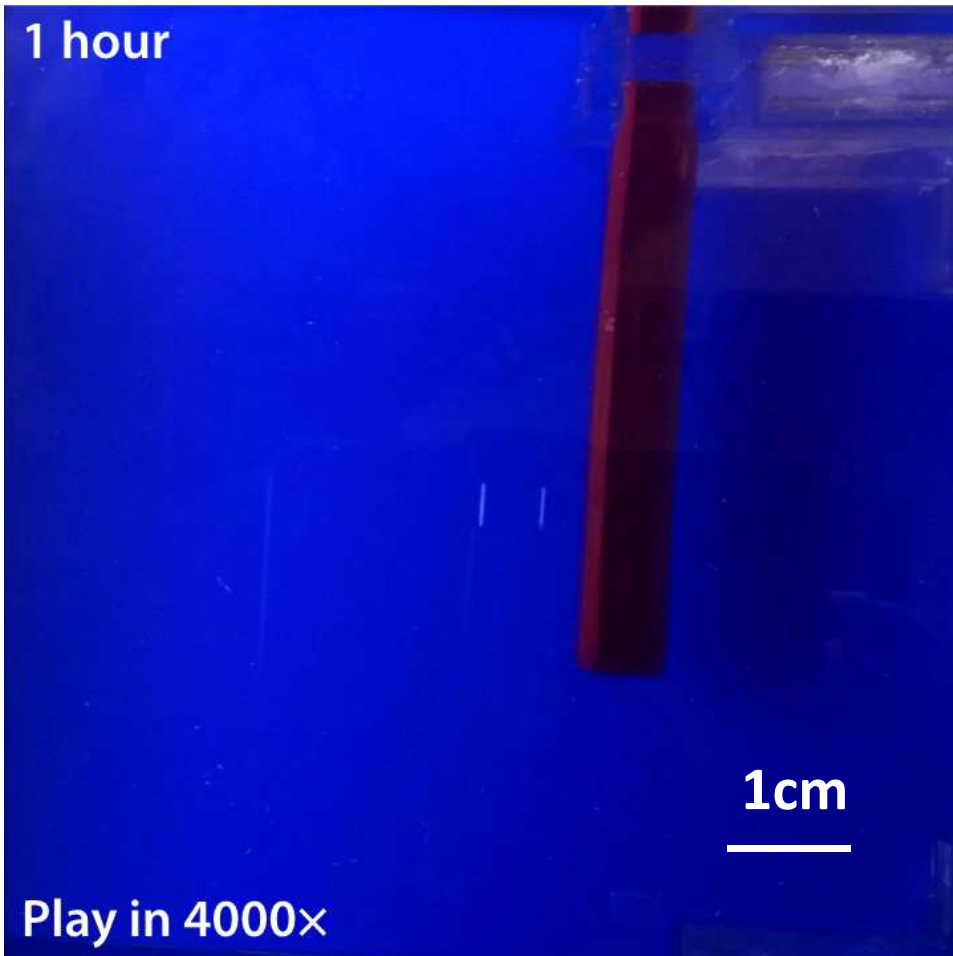
$$\Delta P \sim 100kPa$$

$$L \sim cm$$

$$t_{external} < 1s$$

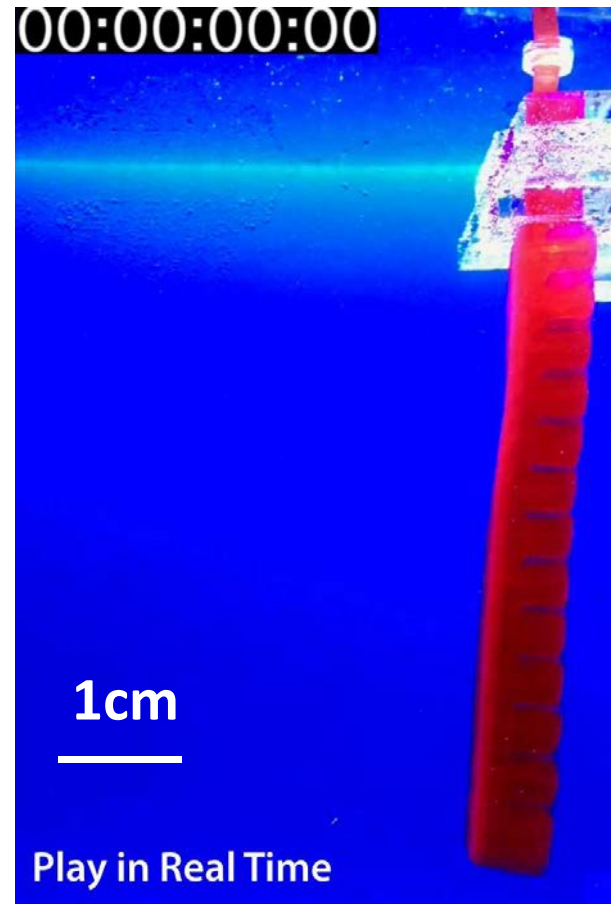
Yuk et al,
Nature Communications,
DOI:10.1038/ncomms14
230 (2017)

Osmotic Actuation

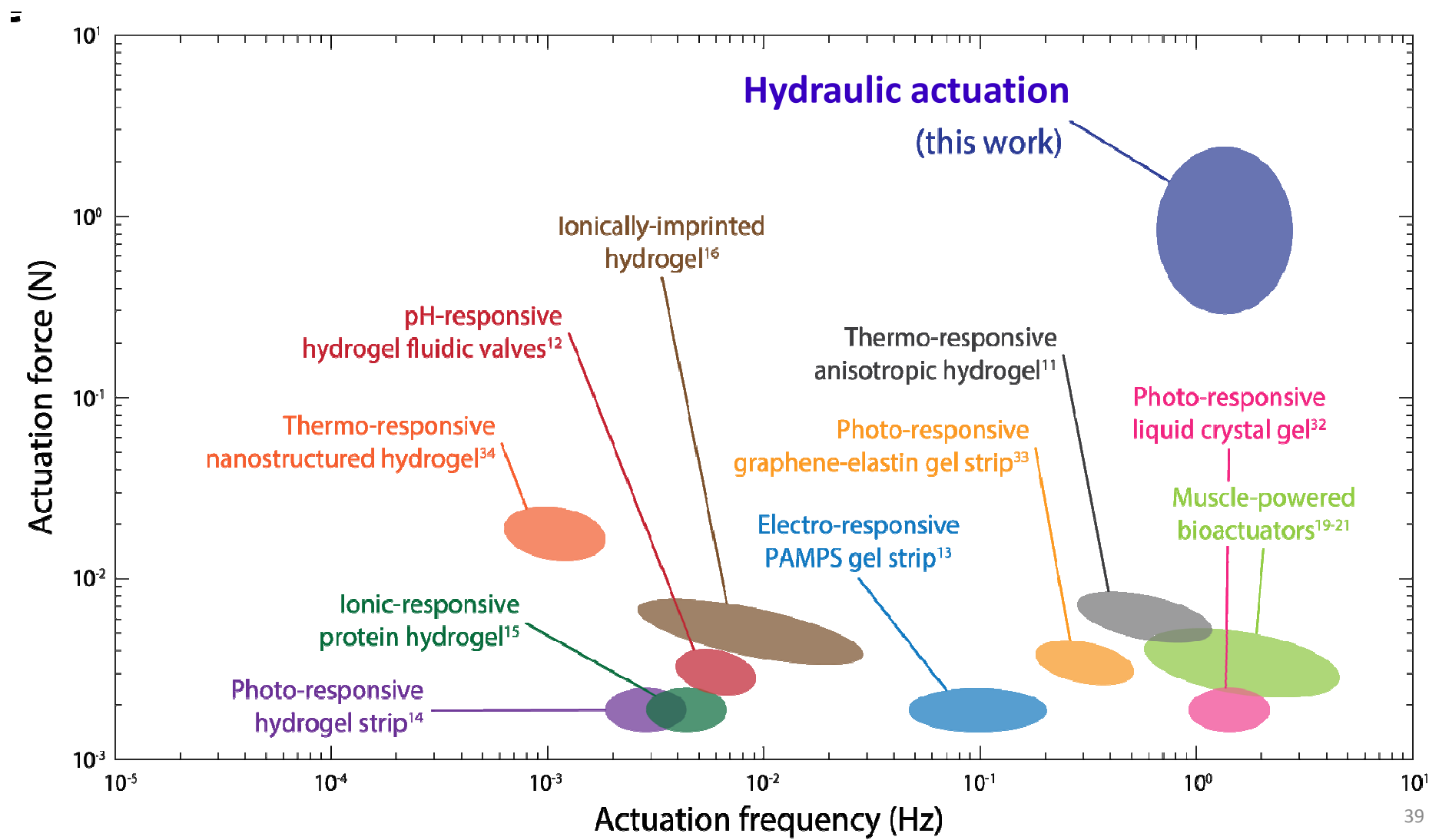


Speed: 4000 X

Hydraulic Actuation



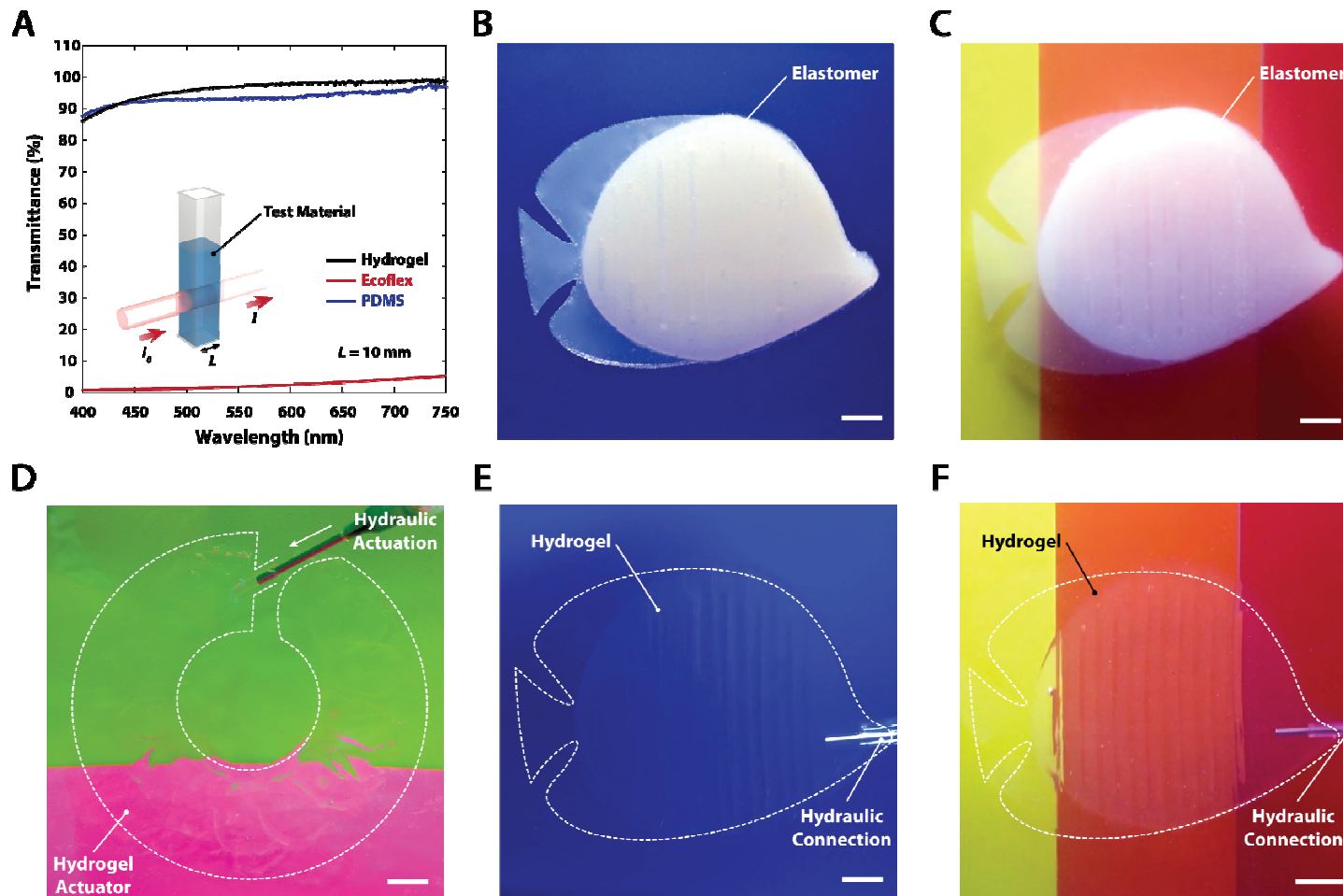
Speed: Real Time



Optically and Acoustically Invisible in Water

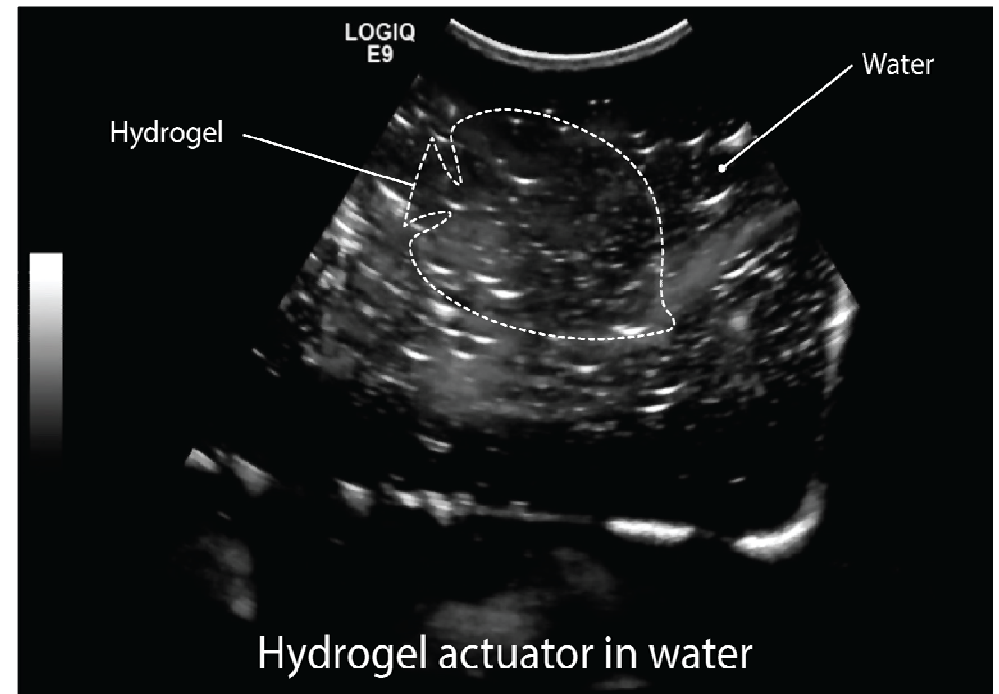
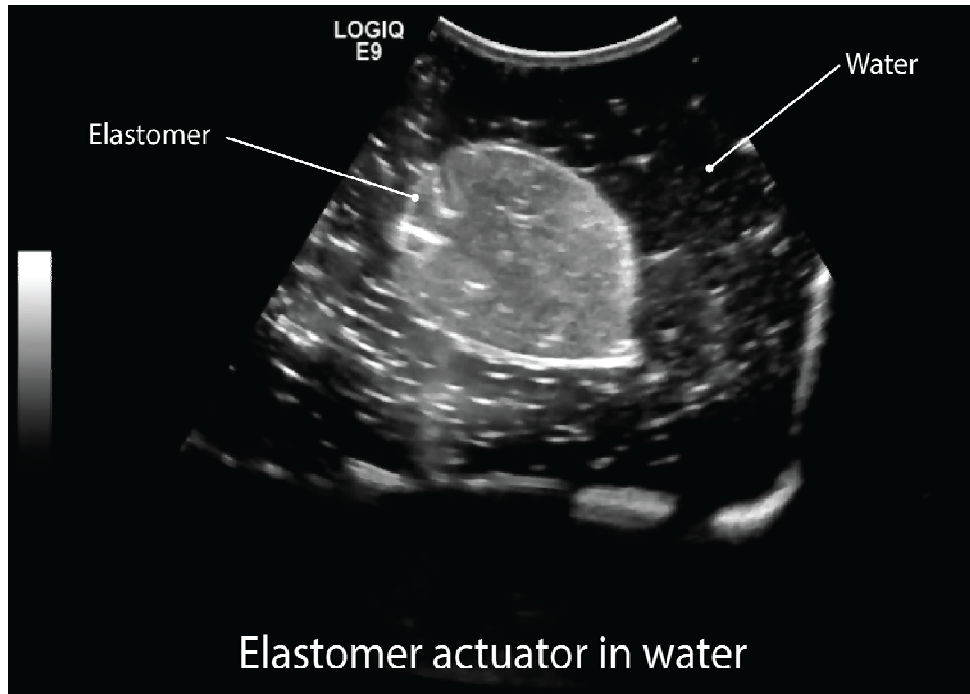
	Water	Hydrogel	Ecoflex	Elastosil	Sylgard 184
n Refractive Index	1.3330	1.3365	N/A [†]	N/A [†]	1.4225
I/I_0 Transmittance (relative to water)	100 %	> 90 %	< 5 %	< 0.1 %	> 90 %
c^{\ddagger} Speed of Sound [m·sec ⁻¹]	1447.5	1485.7	983.4	979.6	1022.4
z_0 Acoustic Impedance [Pa·s·m ⁻¹]	1.448×10^6	1.487×10^6	1.052×10^6	1.058×10^6	1.053×10^6
R Acoustical Reflection Coefficient	0	0.013	0.158	0.156	0.158

Optically and Acoustically Invisible in Water



Yuk et al, Nature Communications, (under revision)

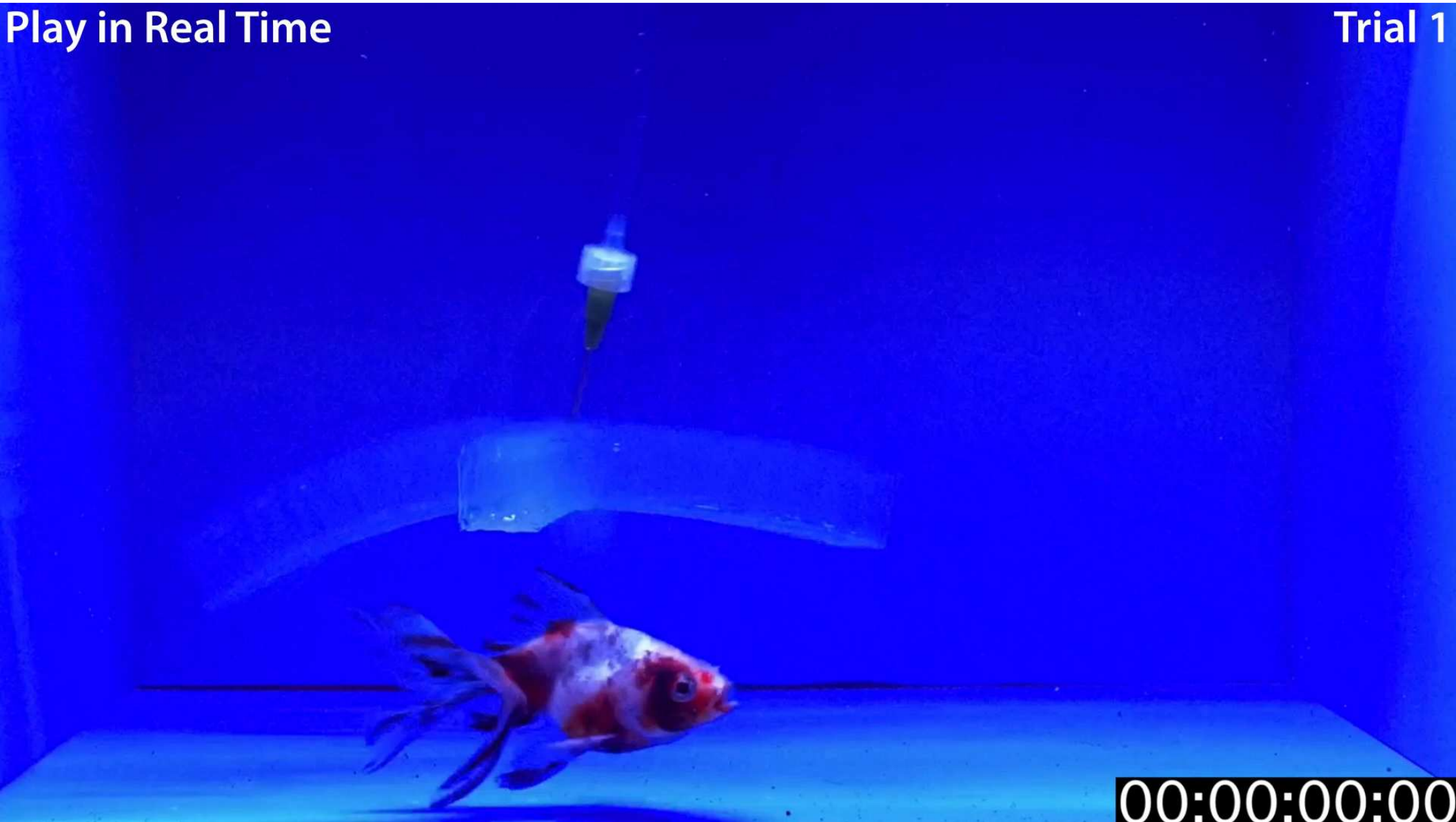
Optically and Acoustically Invisible in Water



Yuk et al, Nature Communications, (under revision)

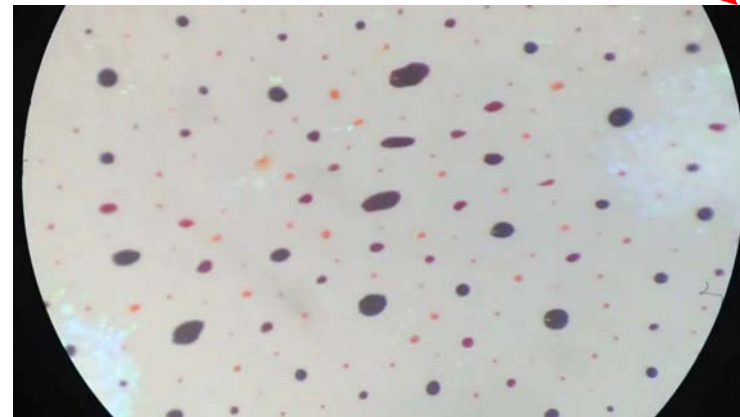
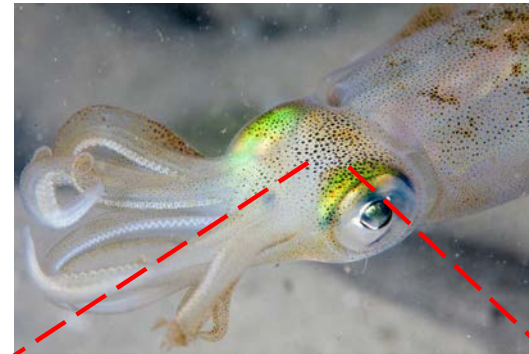
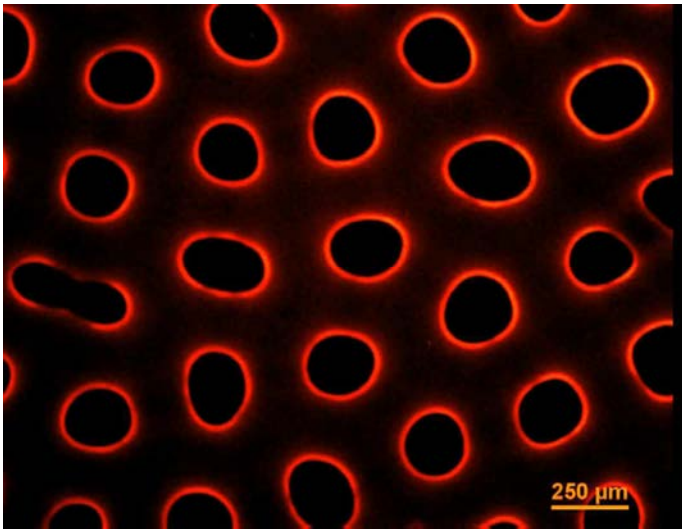
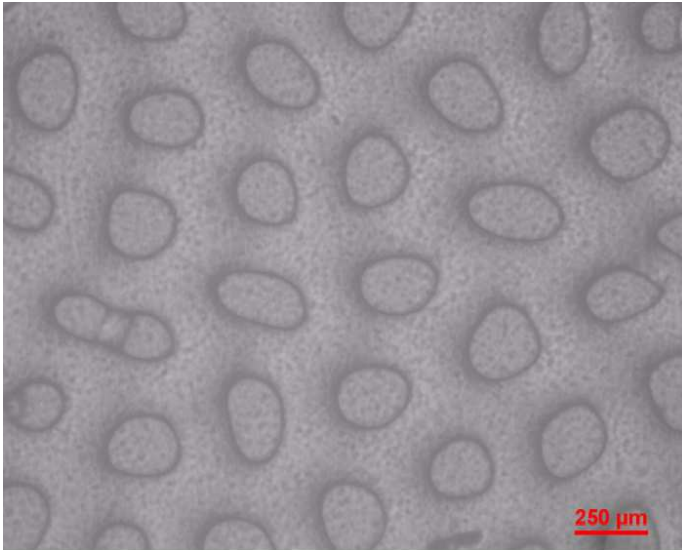
Play in Real Time

Trial 1



00:00:00:00

Synthetic Cephalopod Skin changes Texture and Color.

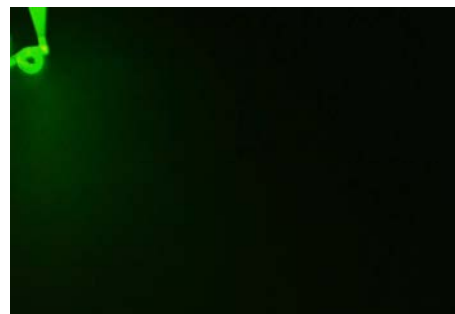
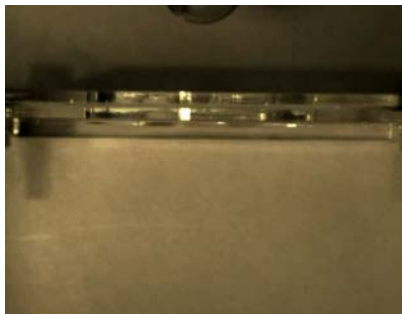


Wang et al, Nature Communications, 5, 4899 (2014)

From Youtube

Unconventional Hydrogels

- **Robust Hydrogels:** Build dissipation into stretchy network.
- **Tough Bonding:** Anchor stretchy network on surface.
- **Manufacturing:** Synthetic biology, 3D printing.
- **Applications:** Scaffolds, Hydrogel electronics, Hydrogel robots



- **More information:** zhaox.org

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Group Members

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- Zhidong Han
- Bin Guo
- Kai Zhang

Previous Members in Academia

- Dr. Qiming Wang (AP, Univ. Southern California)
- Dr. Teng Zhang (AP, Syracuse Univ.)
- Dr. Jianfeng Zang (AP, Huazhong Univ. Sci .Tech.)
- Dr. Gerard-Philippe ZEHIL (AP, Univ. Notre Dame)

Collaborators

- Prof. Lallit Anand, MIT ME
- Prof. David Parks, MIT ME
- Prof. R. Abeyaratne, MIT ME
- Prof. Nick Fang, MIT ME
- Prof. Linda Griffith, MIT BE
- Prof. Tim Lu, MIT BE, EECS
- Prof. Hiroshi Ishii, MIT Media
- Prof. Polina Anikeeva, MIT MSE
- Prof. Tal Cohen, MIT CEE
- Prof. Zhigang Suo, Harvard
- Prof. David Mooney, Harvard
- Prof. Joost Vlassak, Harvard
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Award



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