3D-Printable Hydrogel-Based & Particle-Based Ink Platforms

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Millipore Sigma Webinar
Online
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Disclosure

Prof. Ramille Shah and Dr. Adam Jakus are co-founders of and have financial interests in *Dimension Inx, LLC*, which could potentially benefit from the outcomes of the research and technologies displayed in the following slides.

Let's break down "Additive Manufacturing" and "3D-Printing"

(See ASTM F42)

ENERGY-BASED

"Additive Manufacturing"

Laser Sintering
(Powder Bed)

Laser Melting
(Powder Bed)

Electron Beam Melting
(Powder Bed)

Originally Pioneered by *3D Systems*

Stereolithography
(Monomer Bath)

Instrument Driven

Laser Metal Deposition

DEPOSITION-BASED

"3D-Printing"

Fused Deposition Modeling
(Hot-melt Extrusion)

MakerBot
(now part of 3DS)

Inkjet Binding
(Powder Bed)

Direct Extrusion
(Play-Doh®)

Originally Pioneered by *Stratasys*

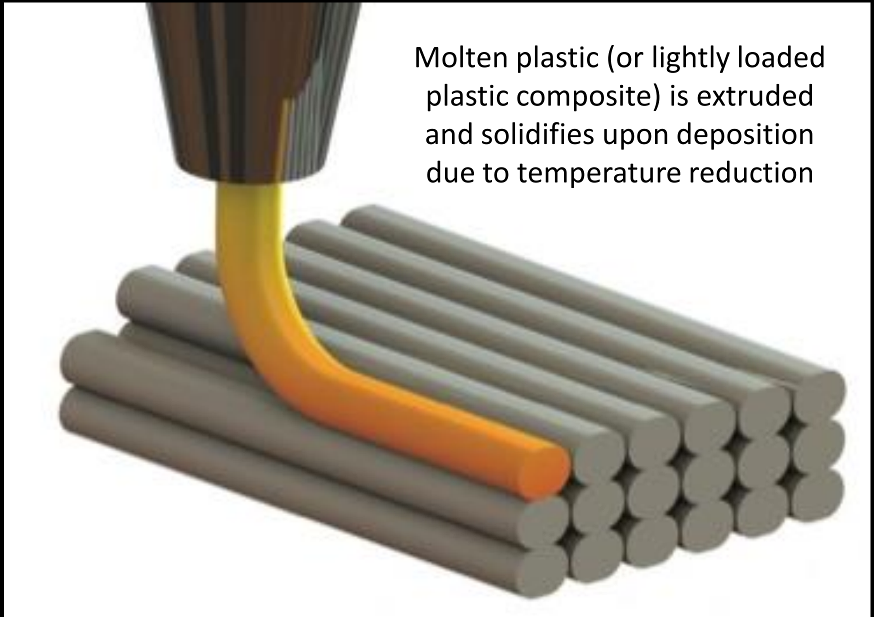
Direct Ink Writing

Materials Driven

PEGX
(Bioprinting)

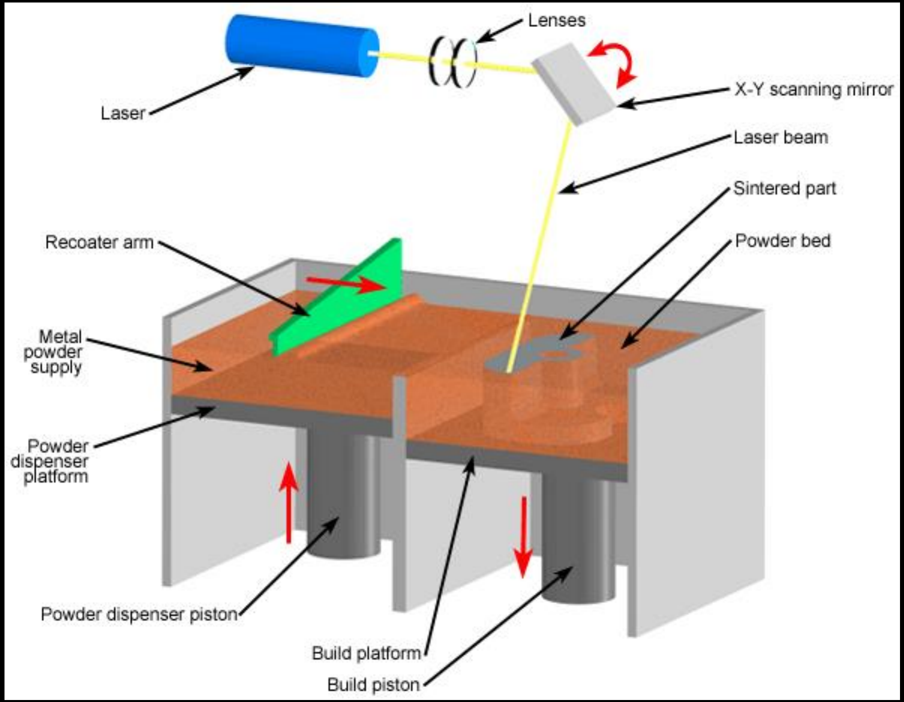
3D-PAINTING

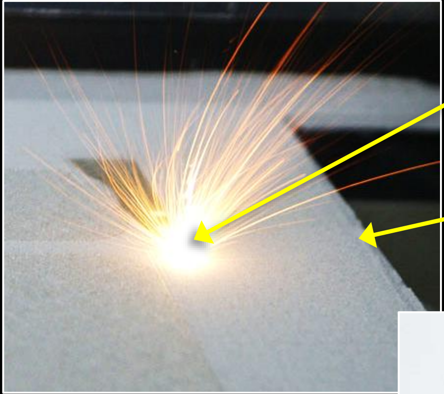
Fused Deposition Modeling: Material Deposition 3D-Printing



Been in use for ~30 years

Energy Beams for Metal Additive Manufacturing

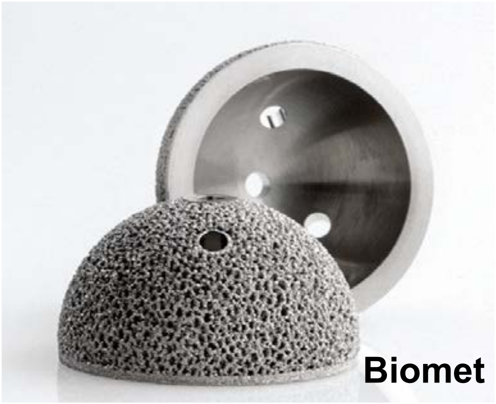


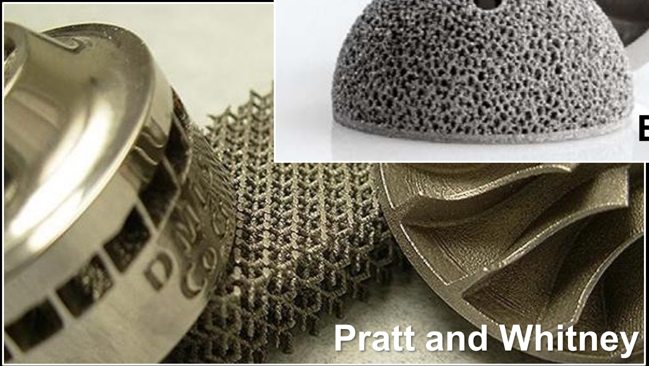


High-power energy beam

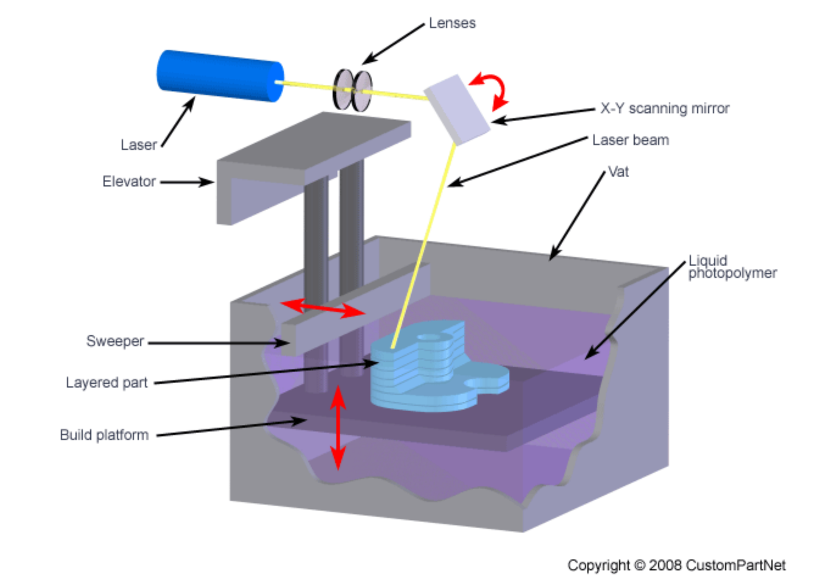
Powder-Bed

Been in use for 30 years





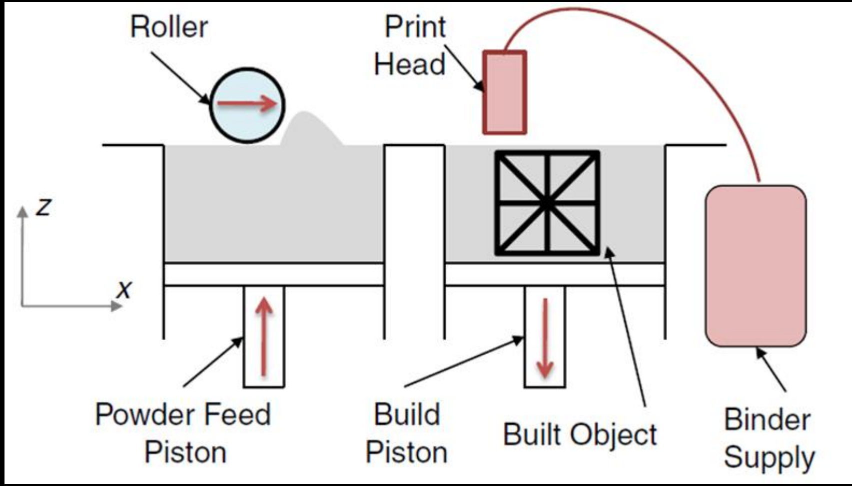
Resin Baths for Photopolymer Additive Manufacturing



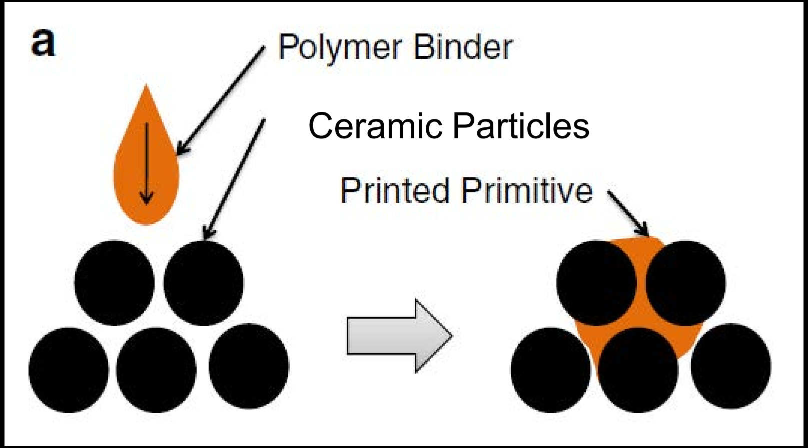
Light selectively polymerizes/cross-links/cures regions of monomer resin bath resulting in selective solidification

Been in use for ~30 years

Inkjet Binding: Powder Bed + Material Deposition



"Glue" Ceramic particles together into a solid "Green Body"



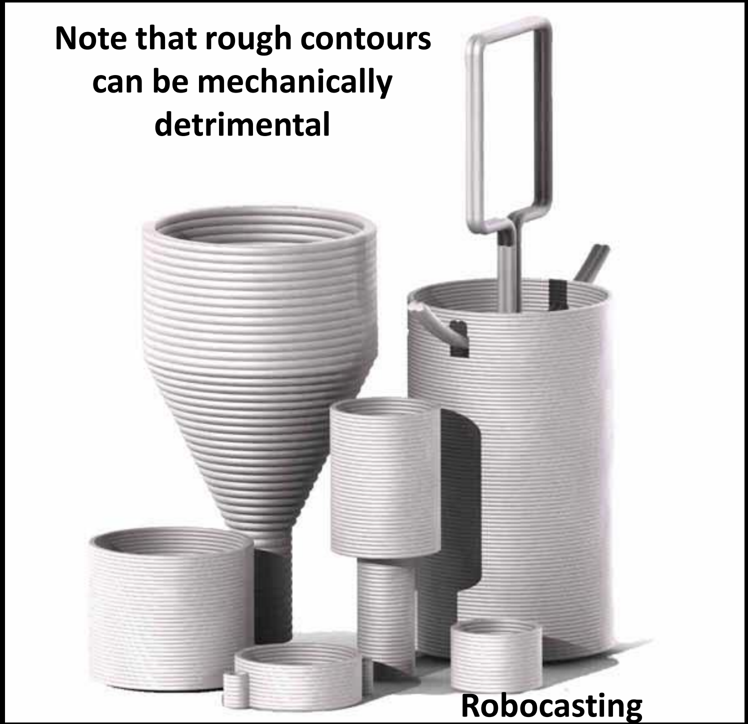
Been in use for ~30 years

C.B. Williams *et al. Int J Adv Manuf Technol*. 53, 2011

Room-Temp. Material Deposition: Direct Ink Writing ("Robocasting")

Been in use for ~20 years

Extruded "Ink" that contains powder and binder and is self-supporting upon deposition. Generally requires post-AM chemical or thermal processing



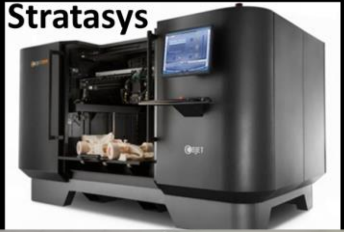
Traditional DIW formulations have been limited to < 40 vol.% powder (typically less than 25 vol.%) → Post-processing difficult

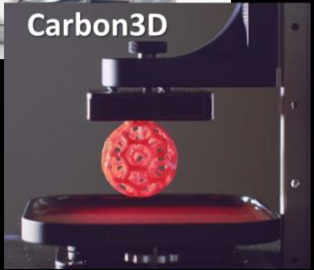
	Equipment	Materials/Consumables
2D-Printing	Two Printer Technologies (inkjet & Laserjet)	Every Color
3D-Printing/Additive Manufacturing	Dozens of technologies and platforms	

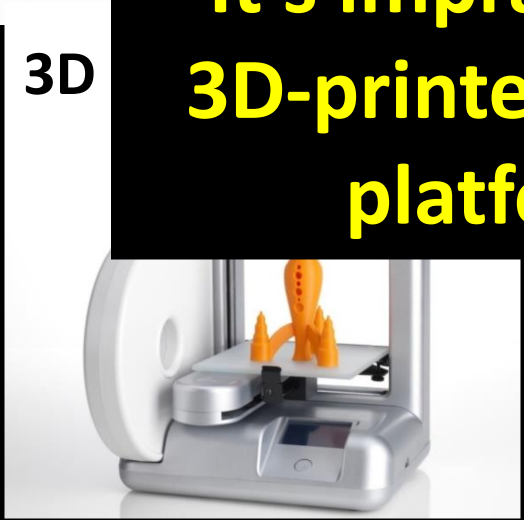
Two Printer Technologies
(inkjet & Laserjet)

Every Color

Dozens of technologies and platforms







It’s impractical to need a different 3D-printer/Additive Manufacturing platform for each material

One Machine → Very Few Materials

Shape

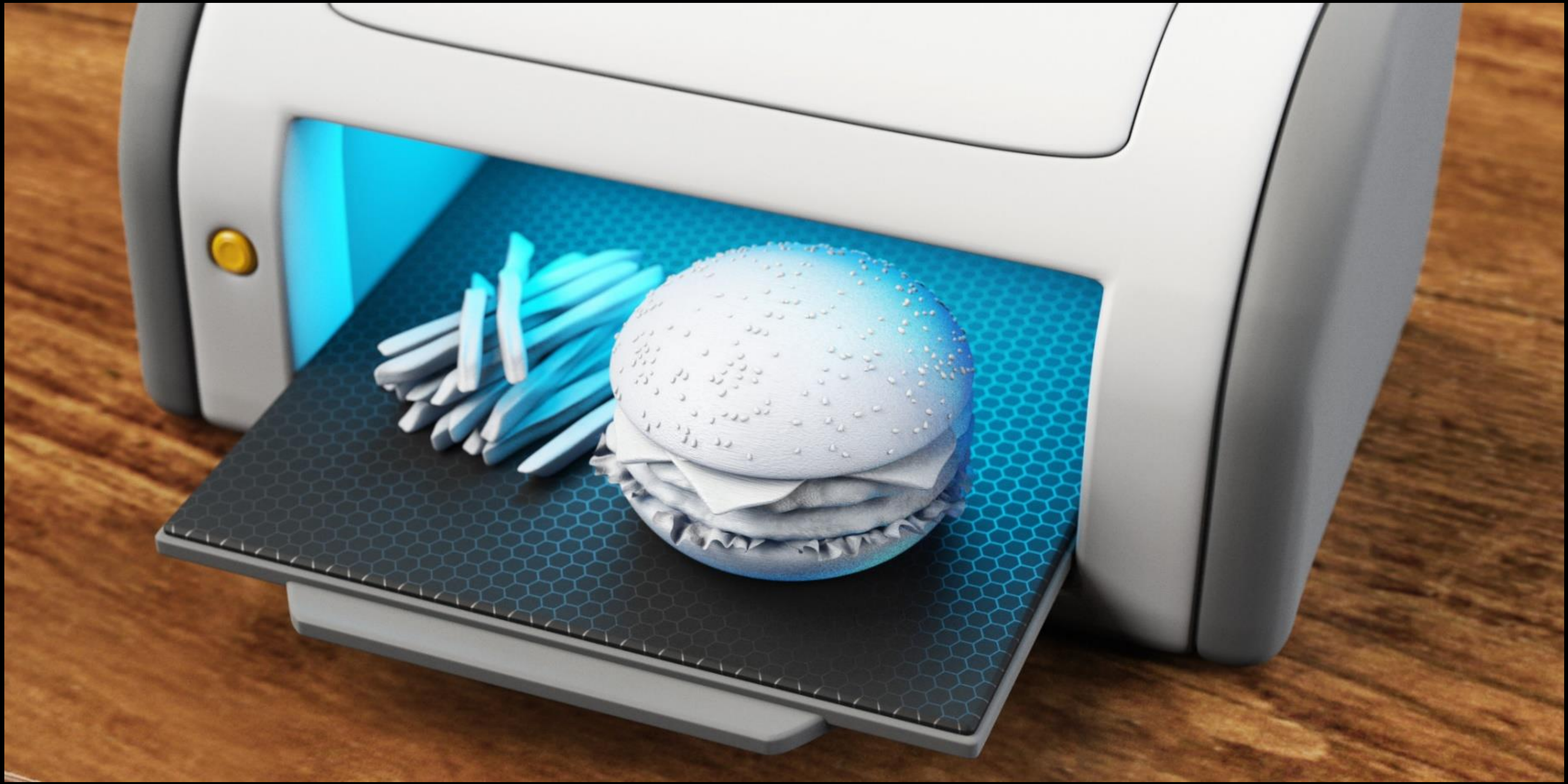
The current specialty of 3DP and AM

Material

Where the most progress is needed
And where the most confusion resides

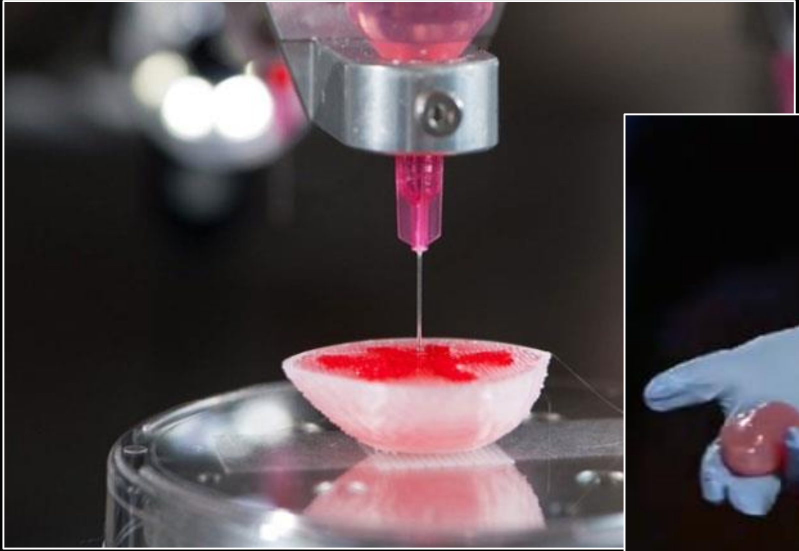
Functionality

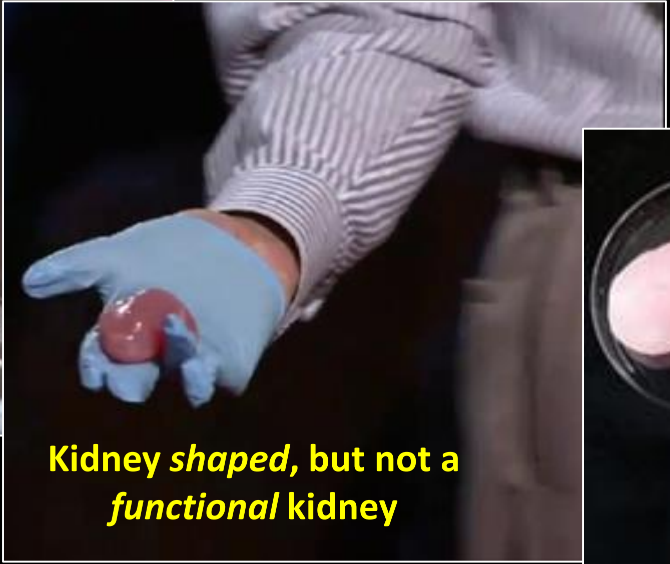
It looks like a burger (shape), but the plastic (material) doesn't taste like a burger (function)!



Huffpost.com

Shape alone ≠ Function

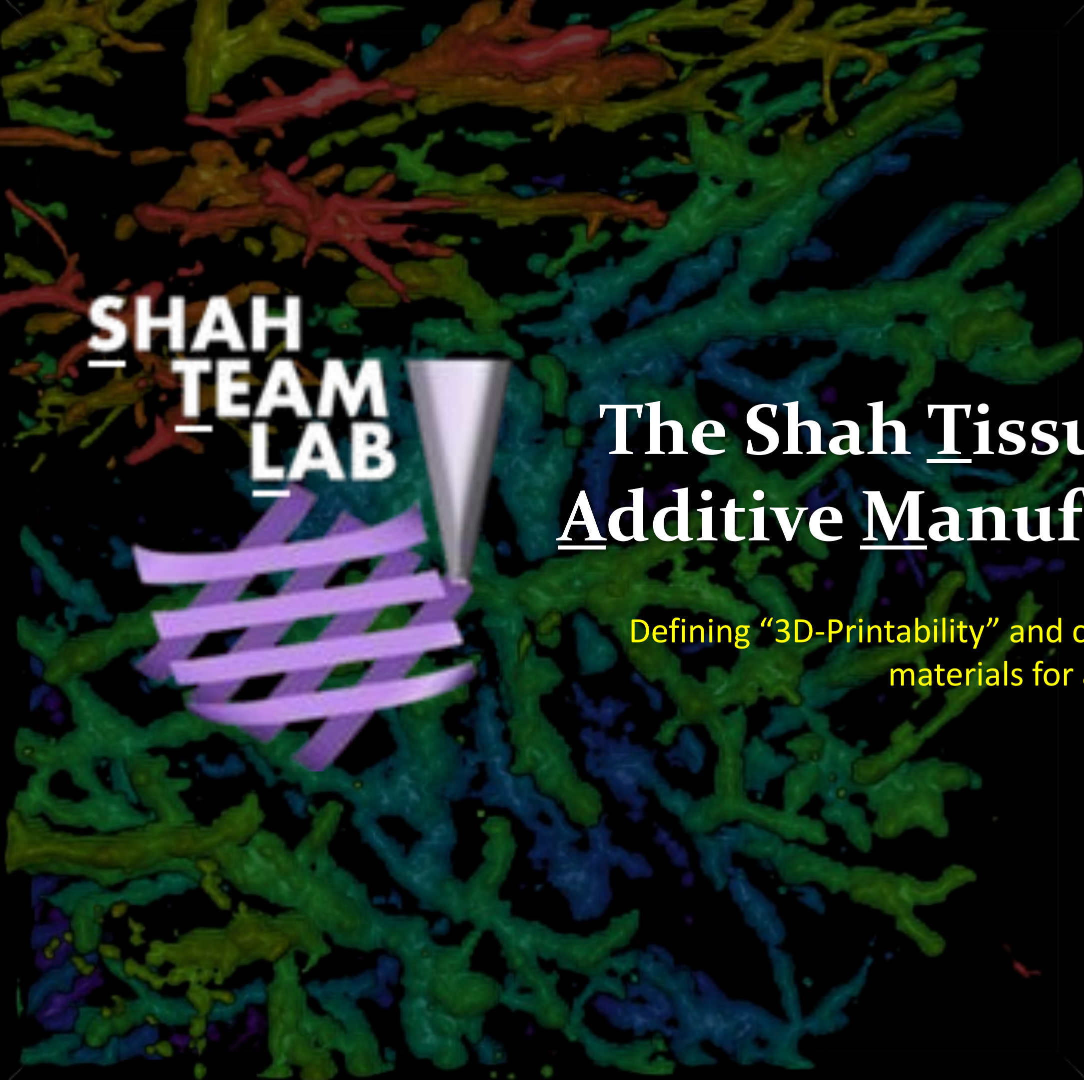




Kidney *shaped*, but not a *functional* kidney

Shaped like organs and tissues, but the *material* is not *functional*

3D-Printing a Human Kidney
TED Talk: March, 2011



The Shah Tissue Engineering and Additive Manufacturing Laboratory

Defining "3D-Printability" and creating and developing new, 3D-printable materials for any and all applications.

SHAH TEAM LAB

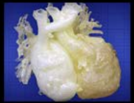
INCREASING: Functionality, Complexity, Regulations, Standards, Etc.

Traditional

Structural

Visual

Guides



Training

Permanent

"TODAY"

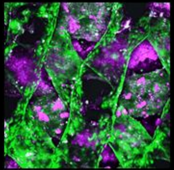
Advanced Biomaterials

"TOMORROW"

Structural/Functional
(Acellular)

Bioprinting

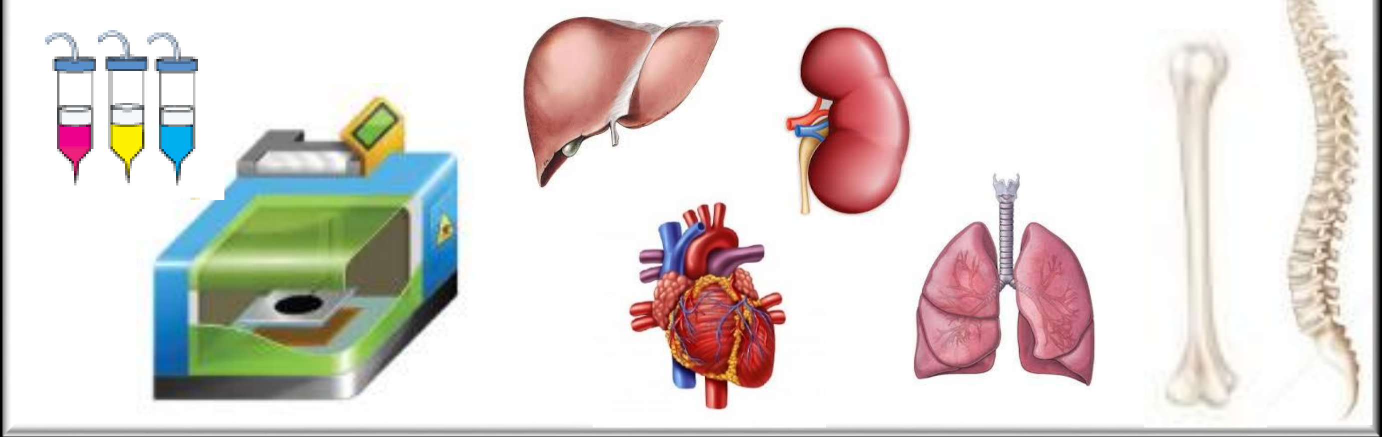
"NEAR FUTURE"



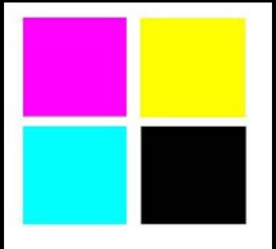
Hydrogels
Functional
(Cellular)

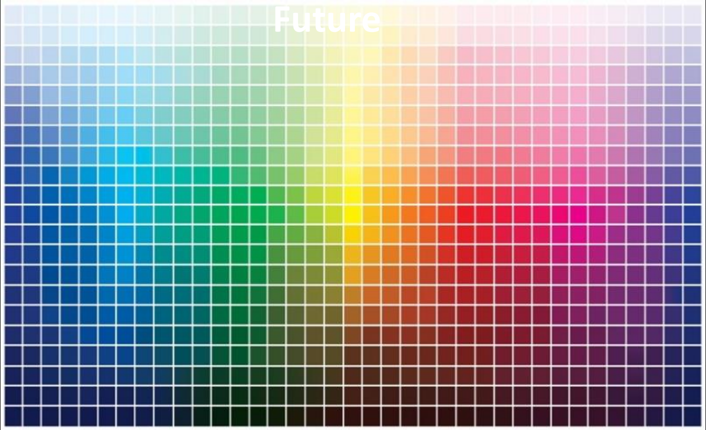
Creating Complex and Versatile 3D Printed Functional Implants

Tissues and organs widely vary in composition, structure, properties, and function.

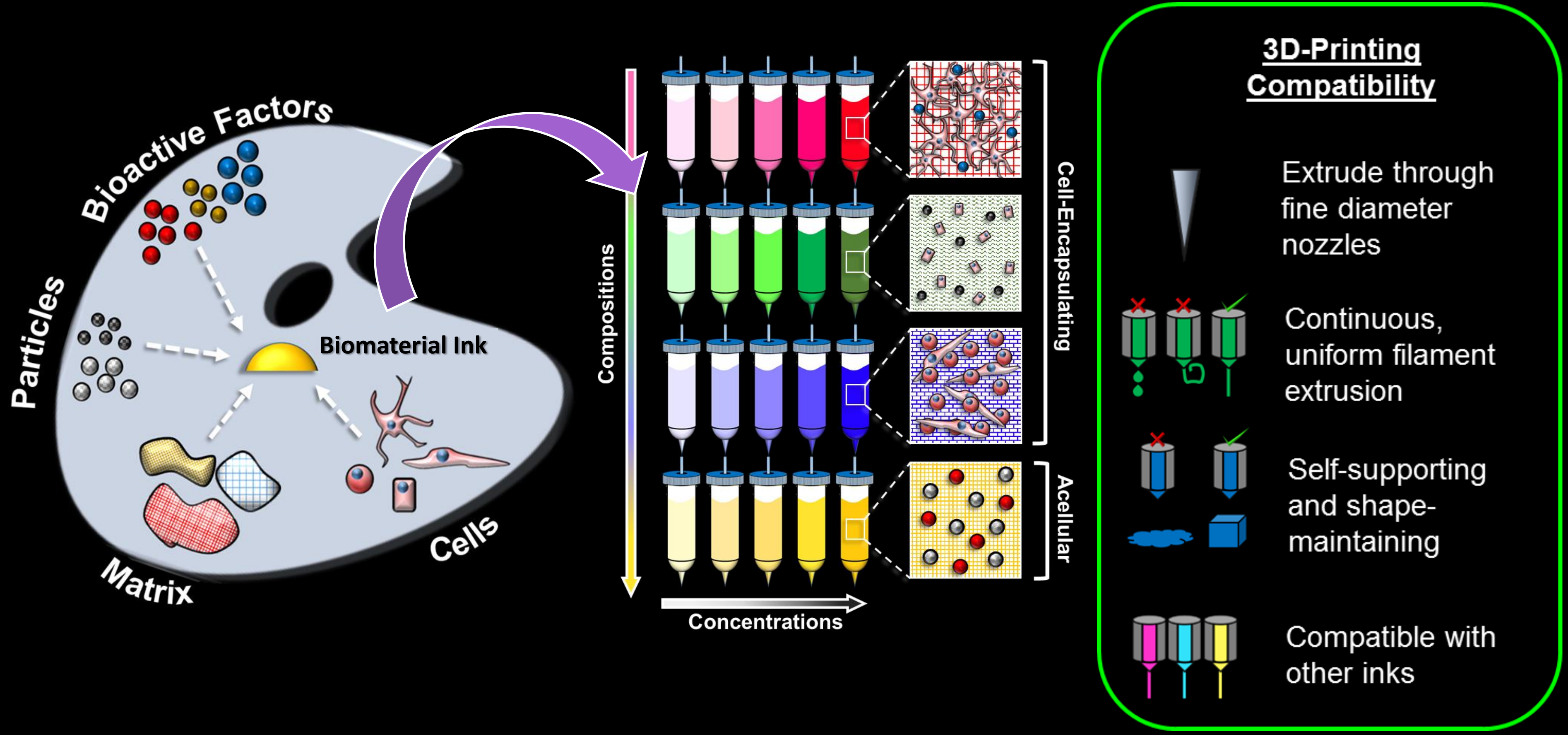


Current





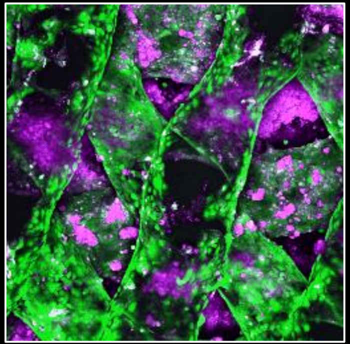
The Biomaterial Ink Palette → 3D-Printable Inks



"Advancing the Field of 3D Biomaterial Printing"
A. Jakus & A. Rutz, R.N. Shah. *Biomedical Materials*; 11(1) *Special Edition. 2016*

Shah TEAM Lab 3D Printable Ink Platforms

Partially Cross-Linked Hydrogel Inks



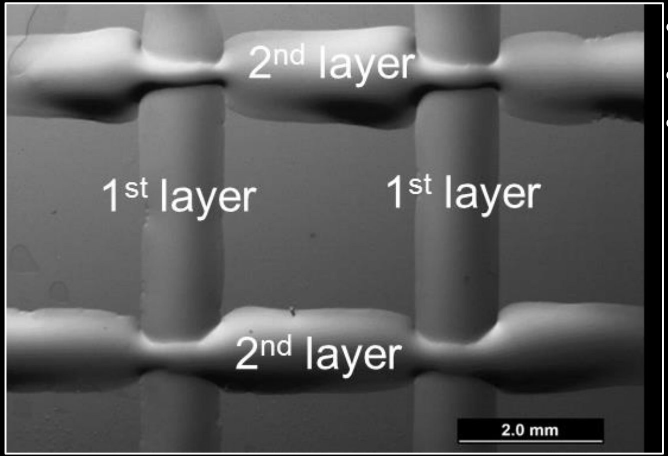
Aqueous-Based, Primarily Water
Hydrophilic
Multi-Mat. Compatible
Can Encapsulate Live Cells (Bioprinting)

Particle-Laden Inks
"3D-Painting"

Well beyond biological and medical applications

Organic Solvent-Based
Primarily Rigid Particles
Multi-Mat. Compatible
Can't Encapsulate Live Cells

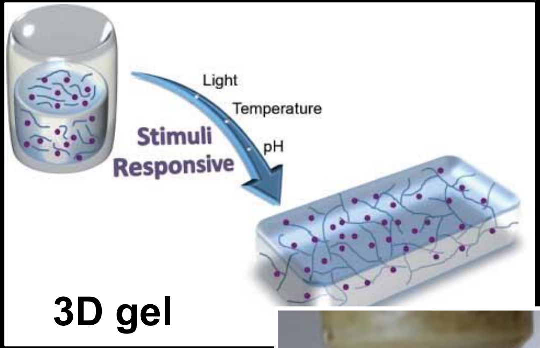
Solution vs. Gel Phase 3D Printing

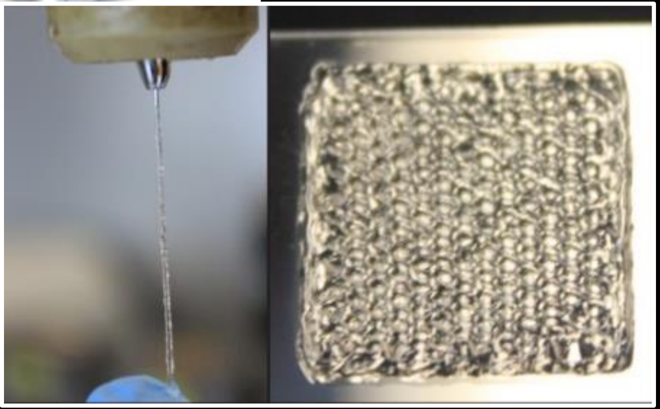


3D-Printing Pre-Gel Solution

Traditional

- Spreading of ink on substrate
- Limited multi-layer fabrication
- Cell settling in the ink (inhomogeneous distribution)

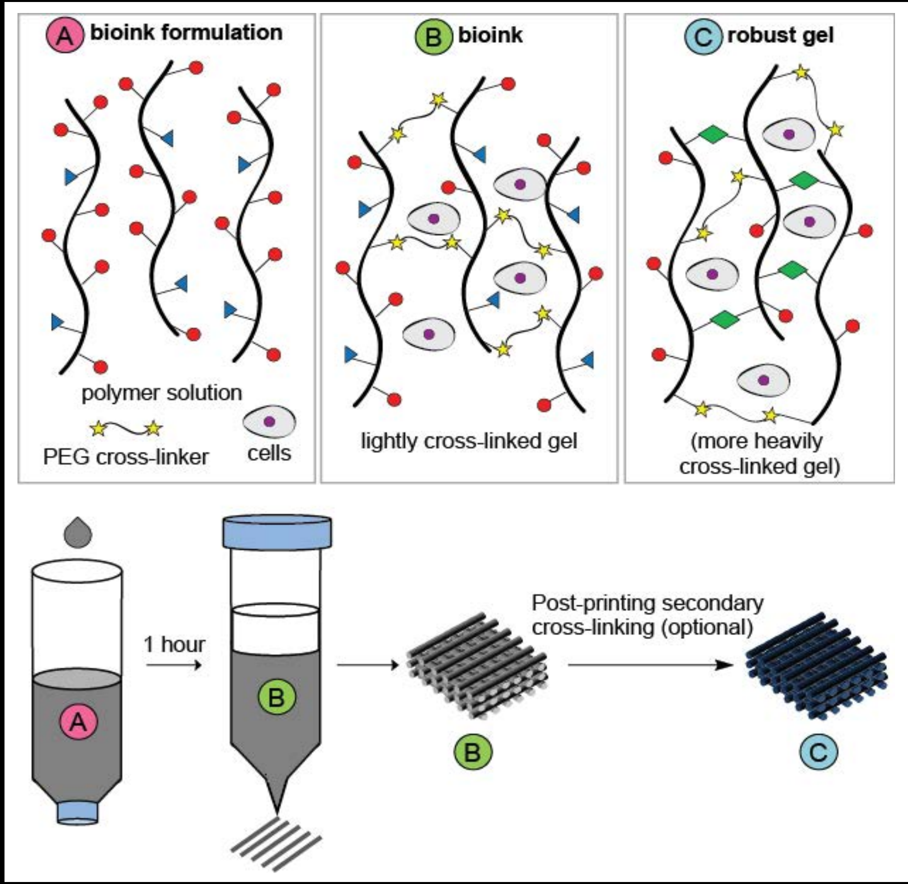




Partially Cross-Linked Hydrogels

Shah TEAM Lab Approach

Developing a Universal Bioink Method: PEGX



Base Polymer:

e.g. Amine -containing

PEG Cross-linker:

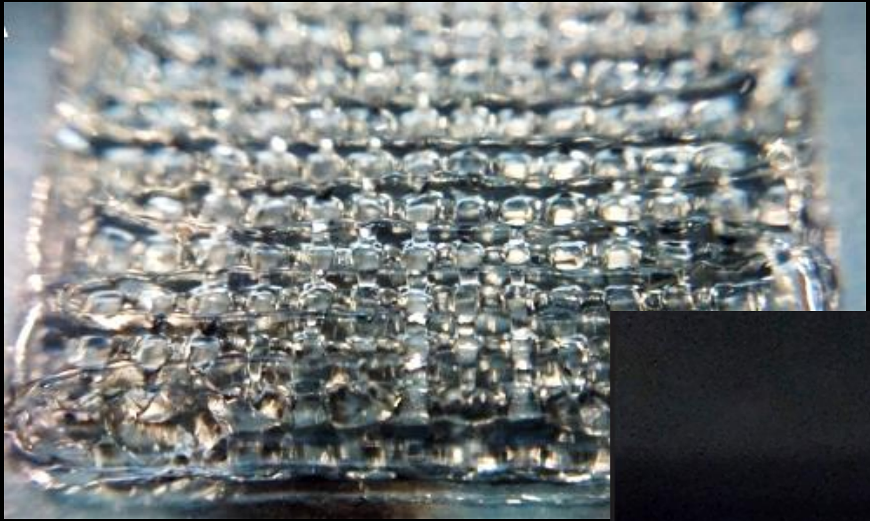
e.g. Homobifunctional NHS (amine-reactive)

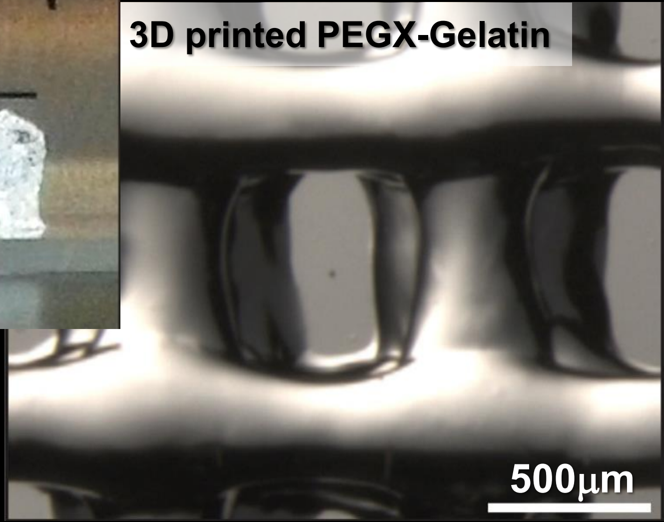
Advantages to PEG:

- *biocompatible*
- *variations in physical and chemical prop. easily accessible*
- *commercially available*
- *inexpensive*

Rutz, Shah et al. *Advanced Materials*, 27(9), **2015**

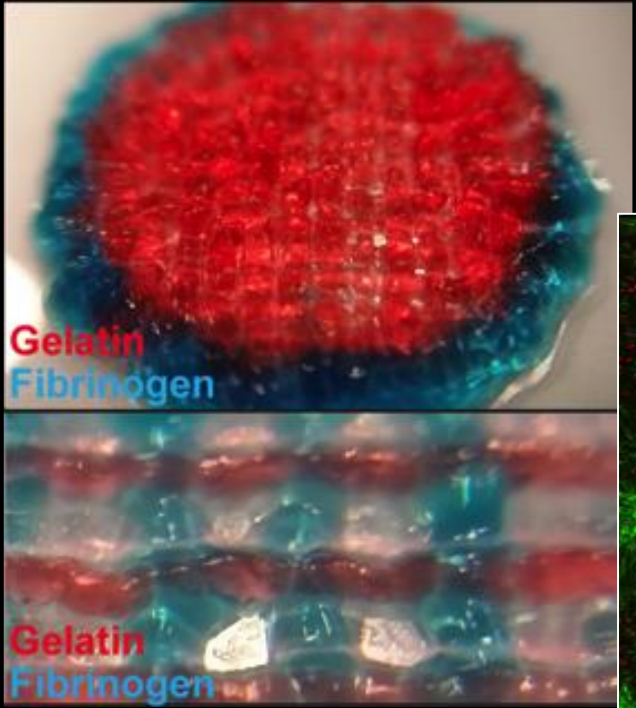
3D Printed PEGX-Gelatin



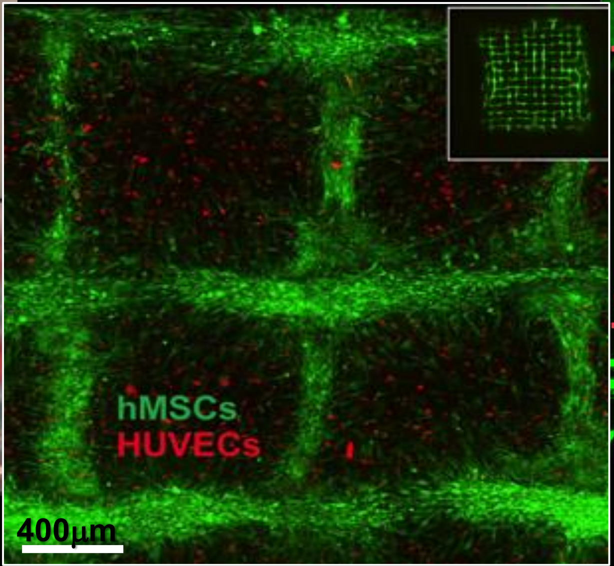


Multi-Material Printing and Cell Patterning

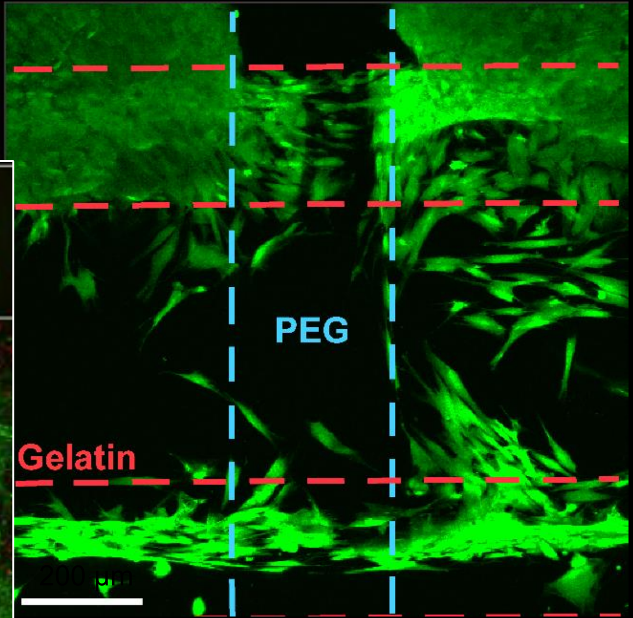
Co-printing protein bioinks for multi-ECM constructs



Cell Patterning

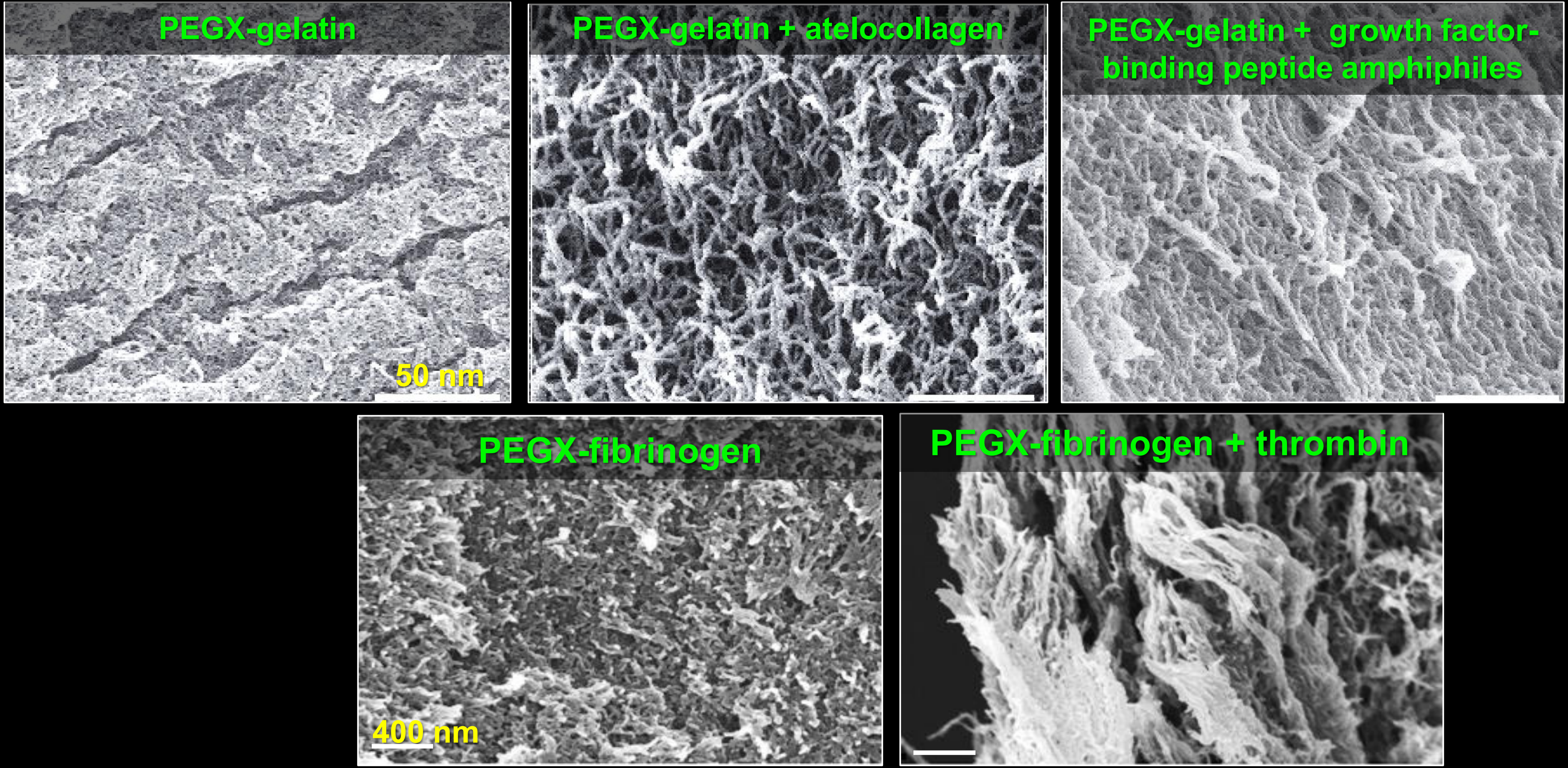


Co-printing natural and synthetic bioinks to control cell adhesion in 3D



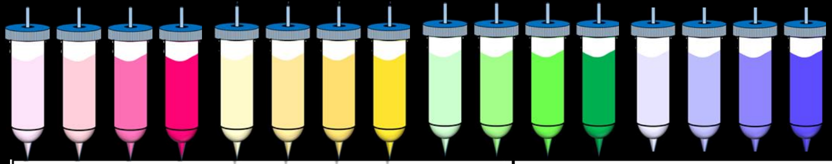
Rutz, Shah et al. *Advanced Materials,* 27(9), **2015**

Customizing Nanostructure and Bioactivity

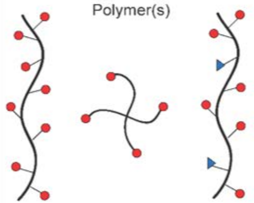


Rutz, Shah et al. *Advanced Materials*, 27(9), **2015**

An Expansive Variety of Soft Material Properties



Base Polymer



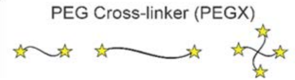
Natural
- gelatin
- gelatin methacrylate
- fibrinogen

Synthetic
- 4 arm PEG amine
- 4 arm PEG thiol

Natural Mixtures
- gelatin and fibrinogen
- gelatin and atelocollagen

Synthetic-Natural Mixtures
- gelatin and 4 arm PEG amine
- gelatin and peptide amphiphiles

PEGX



Linear
- 1k, 5k,10k g/mol

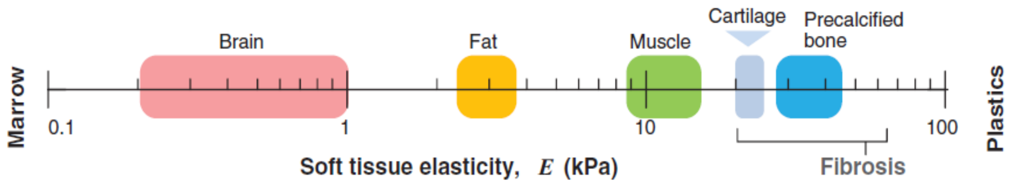
4 arm
- 10k, 20k g/mol

8 arm
- 40kg/mol

Cross-linking Chemistry

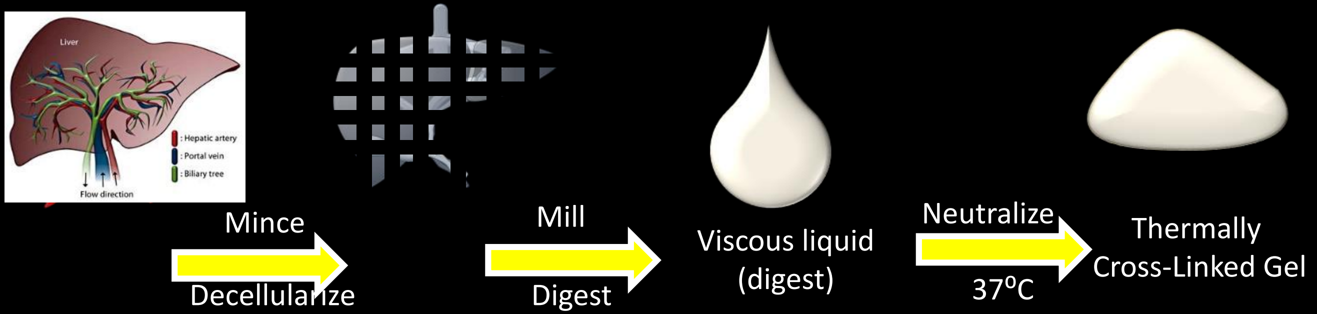
- NHS ester + Amine
- Maleimide + Thiol
- Vinyl sulfone + Thiol
- Acrylate + Thiol

- *Over 100 formulations from a variety of materials - natural and synthetic*
- *Can customize 3D printed material composition, bioactivity, nanostructure, degradation, & mechanical properties - without compromising printability*
- *Achieve 3D printable hydrogel constructs over a range of 500Pa – 40kPa*

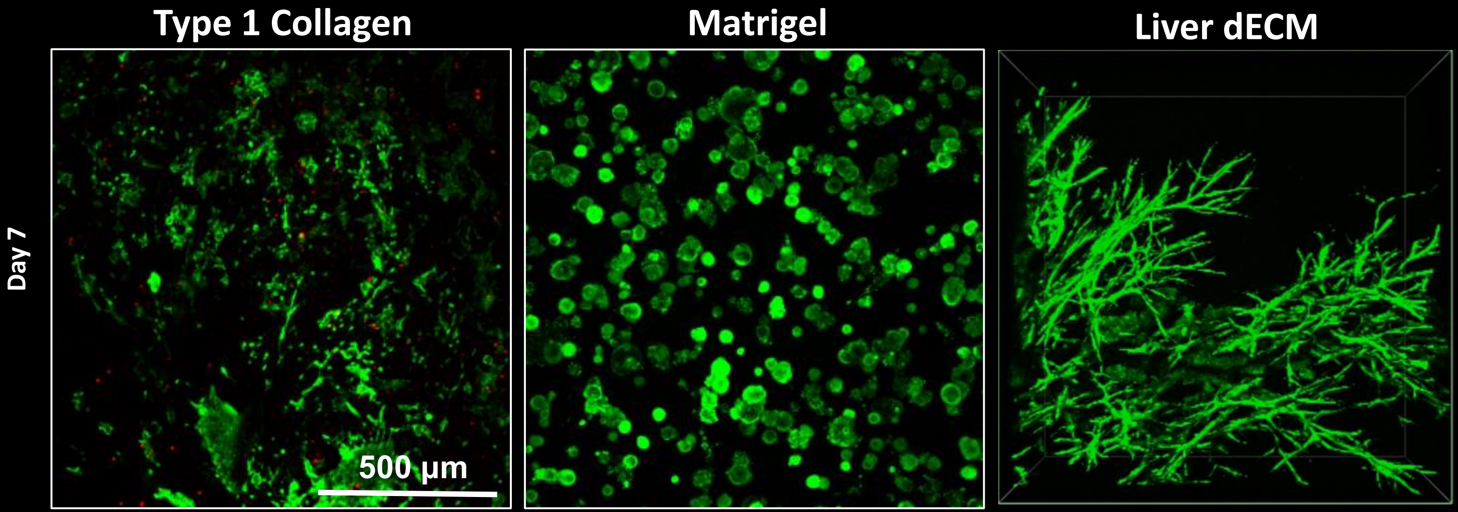


Discher et al. *Science*. **2009**.

Enhancing Bioactivity w/ Tissue Specific Decellularized ECM



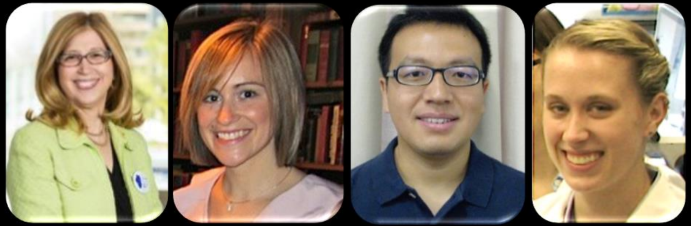
Cholangiocytes: biliary epithelial cells



Engineering a Bioprosthetic Ovary: Addressing Gonadotoxicity or Gonadal Dysfunction

- Significant correlation between radiation therapy and infertility, acute ovarian failure, and low hormone levels in female cancer survivors

<u>Our Solution:</u>
Isolate and culture follicles from patient before treatment in a Bioprosthetic Ovary and implant back into patient after treatment to preserve fertility and hormone function



Prof. Teresa Woodruff, Dr. Monica Laronda, Dr. Shuo Xiao, Kelly Whelan

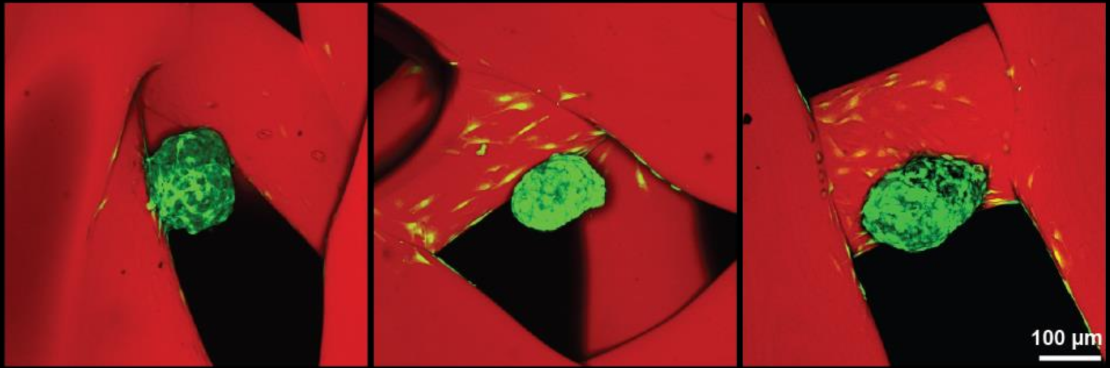
Effect of Pore Geometry on Follicle Survival

Day 2

30° 60° 90°

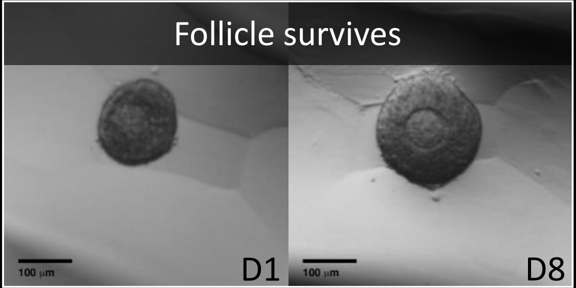
gelatin scaffold

follicle

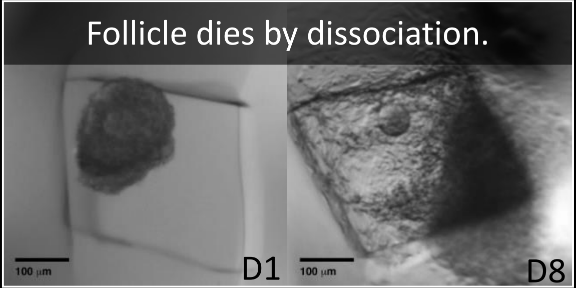


Day 8

corner



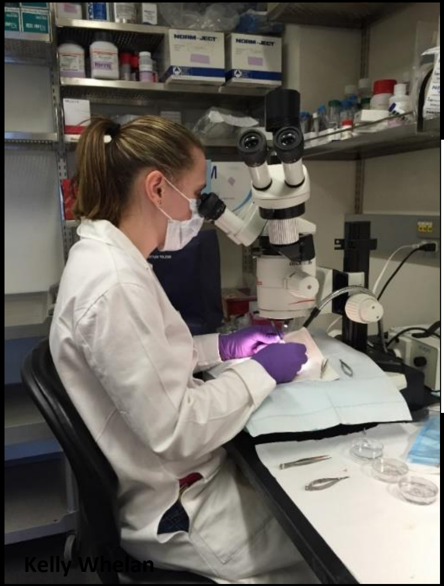
contacting only 1 strut

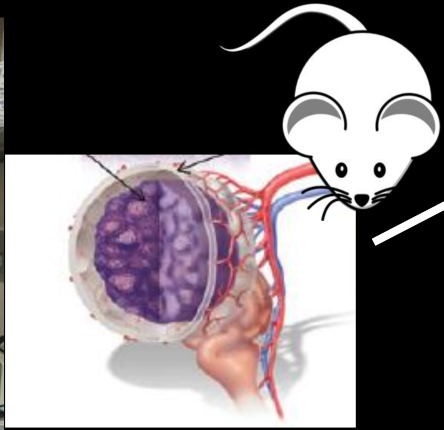


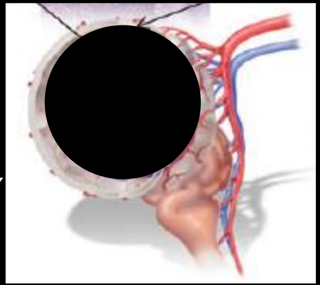
Increasing number of contacts decreases follicle spreading and maintains spherical shape necessary for survival

Rutz and Laronda, Woodruff, Shah et al. *Nature Communications.* 8, 15261. 2017

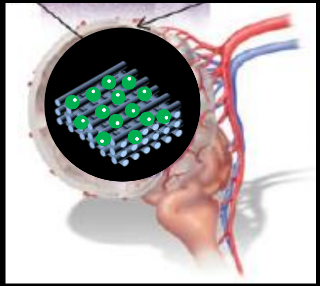
GFP+ Follicle-Seeded 3D Printed Scaffold Implantation





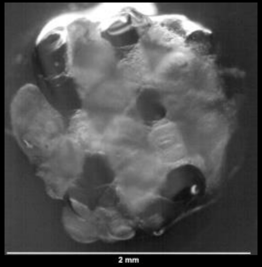


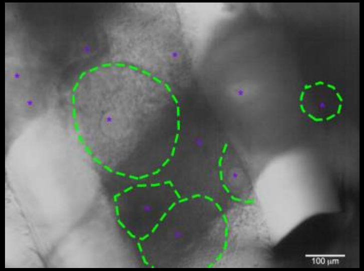
1. Ovarian tissue is removed



2. Bioprosthetic ovary implanted

Bioprosthetic Ovary = GFP+ follicles on 3D printed gelatin scaffold

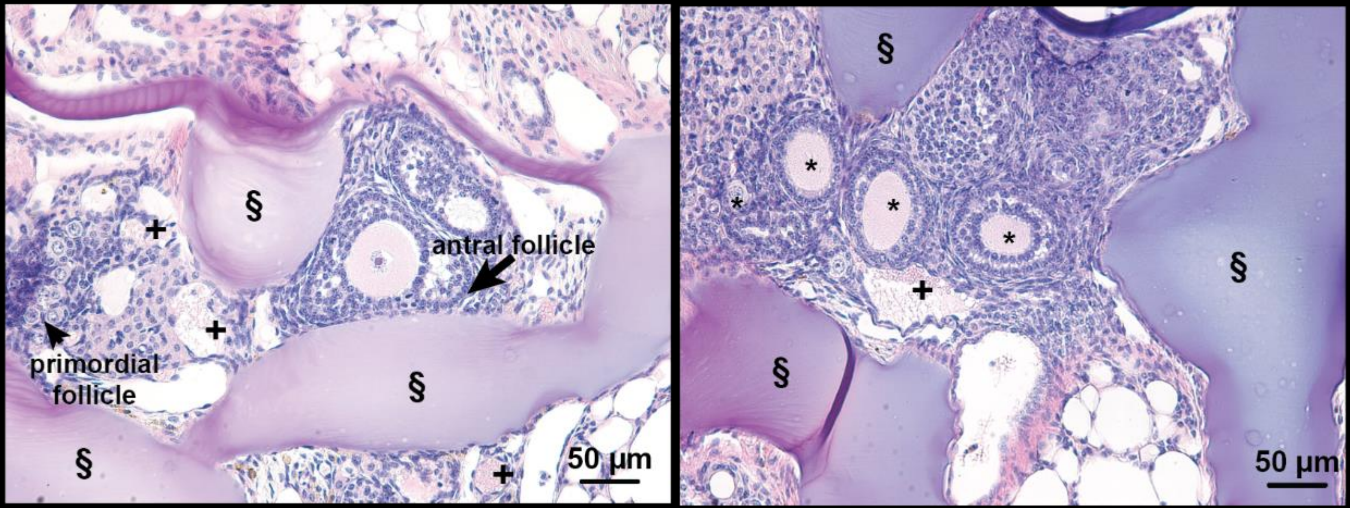


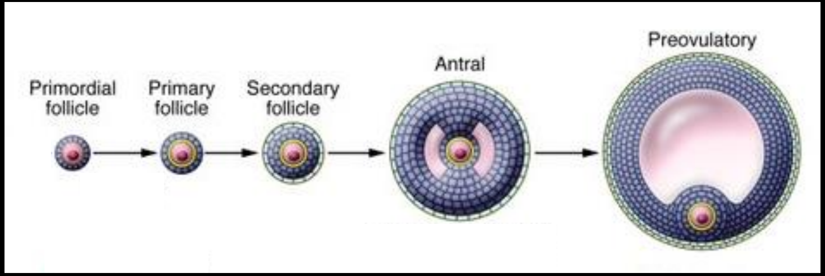


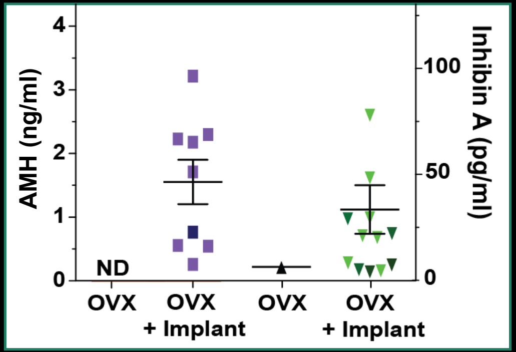
Rutz and Laronda, Woodruff, Shah et al. *Nature Communications.* 8, 15261. 2017

Folliculogenesis & Hormone Production Restored

§, scaffold strut. **+**, vessels.



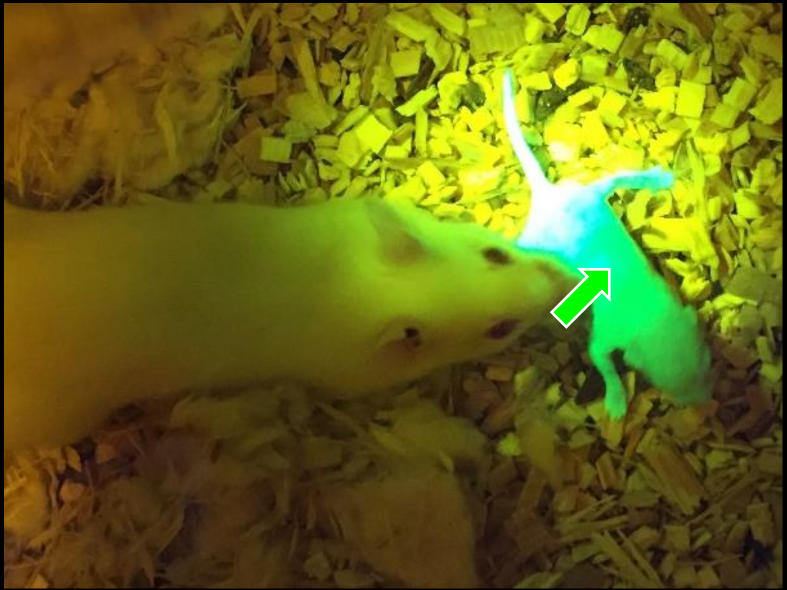




Rutz and Laronda, Woodruff, Shah et al. *Nature Communications.* 8, 15261. 2017

Fertility Restoration: In Vivo Live Birth and Lactation

Bioprosthesis-Derived Pup



Lactating Mom

Control Female

Milk belly

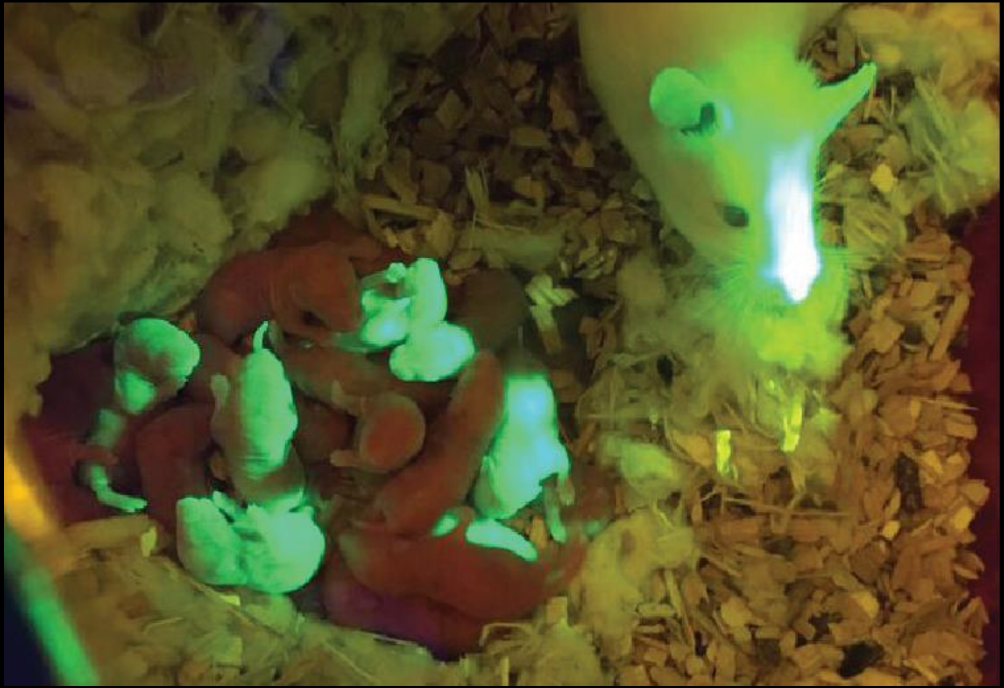
Successful live birth of GFP+ offspring

Pups raised by mom until weening; mom lactated and was hormonally functional

Rutz and Laronda, Woodruff, Shah et al. *Nature Communications.* 8, 15261. 2017

Fertility Restoration: In Vivo Live Birth and Lactation

Bioprosthesis-Derived Grandpups



Pup grew to adulthood, was mated and had pups – had normal fertility

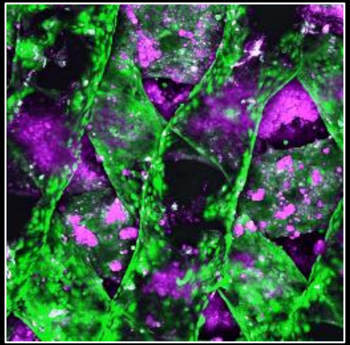
First demonstration of a functional implanted organ created via 3D printing

In the midst of setting up a 3D printing center within hospital GMP facility to produce 3D printed hydrogel scaffolds for future preclinical (porcine) & clinical trials

Rutz and Laronda, Woodruff, Shah et al. *Nature Communications.* 8, 15261. 2017

Shah TEAM Lab 3D Printable Ink Platforms

Partially Cross-Linked Hydrogel Inks



Aqueous-Based, Primarily Water
Hydrophilic
Multi-Mat. Compatible
Can Encapsulate Live Cells (Bioprinting)

Particle-Laden Inks

“3D-Painting”

Well beyond biological and medical applications

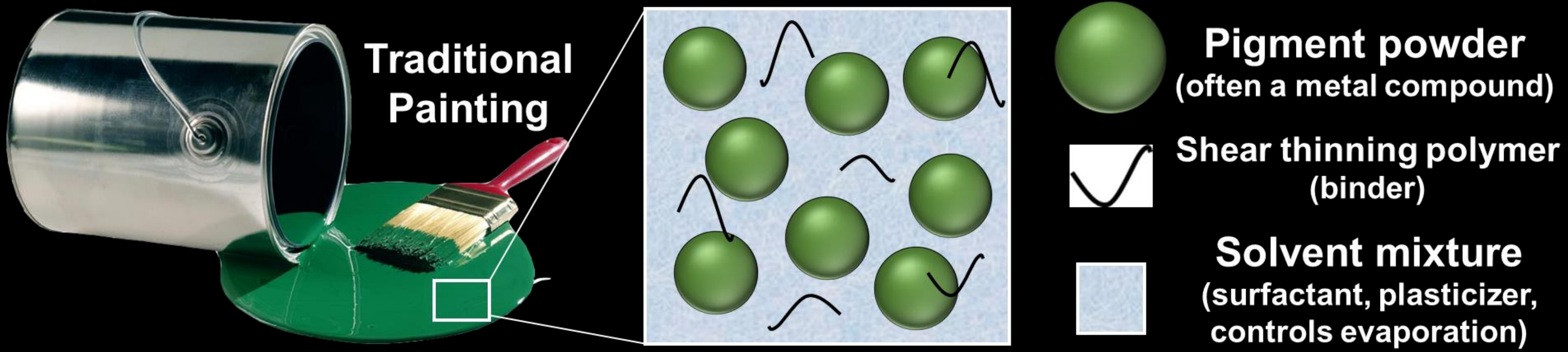
Organic Solvent-Based
Primarily Rigid Particles
Multi-Mat. Compatible
Can’t Encapsulate Live Cells

3D-Painting: A Comprehensive, Materials-Centric Approach to 3D-Printing & Additive Manufacturing

Not just different colors... Completely different materials!

A selection of more than 300 distinct 3D-Paints developed by the Shah TEAM Lab
(...and can be infinitely mixed and modified)

Why "3D-Painting": Let's Take a Closer Look at Paint...



It's really quite interesting!

(but terribly boring to watch dry)

Solvents slowly evaporate and we get a solid layer of “colored particles” embedded in polymer

=

A solid two-dimensional layer

Inorganic pigment

But this is a slow process…

"Frankly, I think watching paint dry has been given a bad press."

3D-Painting: Watching paint dry has never been so much fun!

Room-temperature deposition

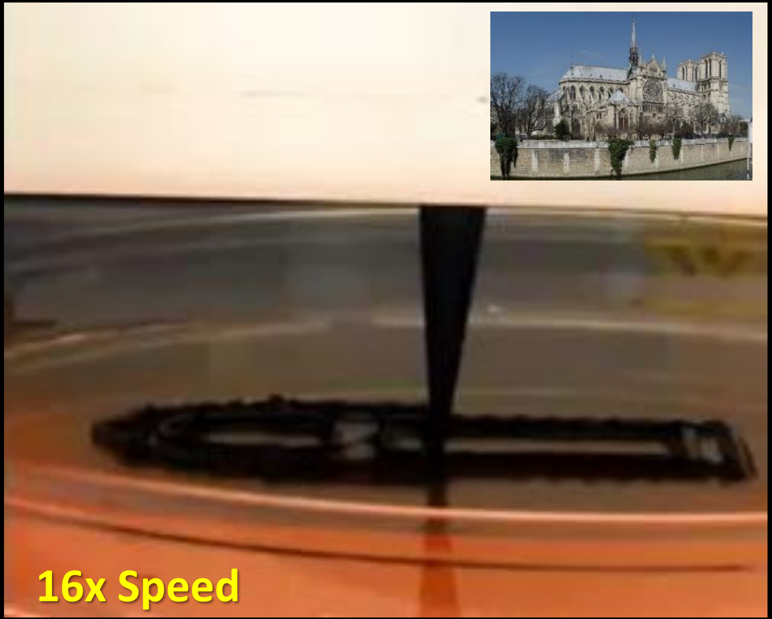
Deposition rates up to 150 mm/s*

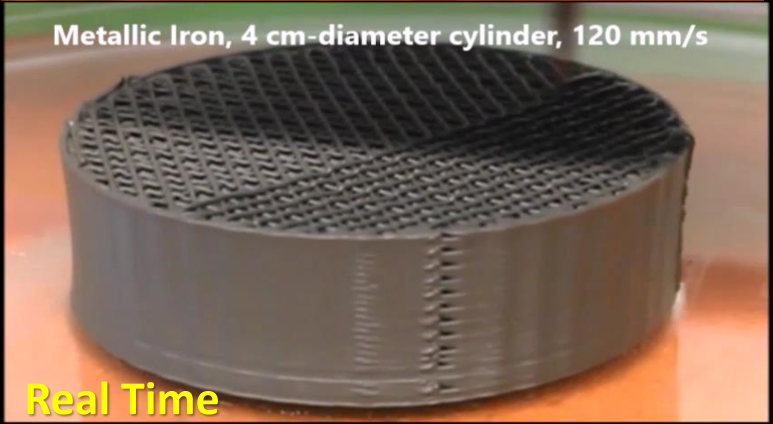
No powder beds or resin baths
No Support materials required
No curing or post-reactions to stabilize structures

Objects can be handled immediately

One to thousands of layers

100 µm to 1.4 cm** fiber diameter

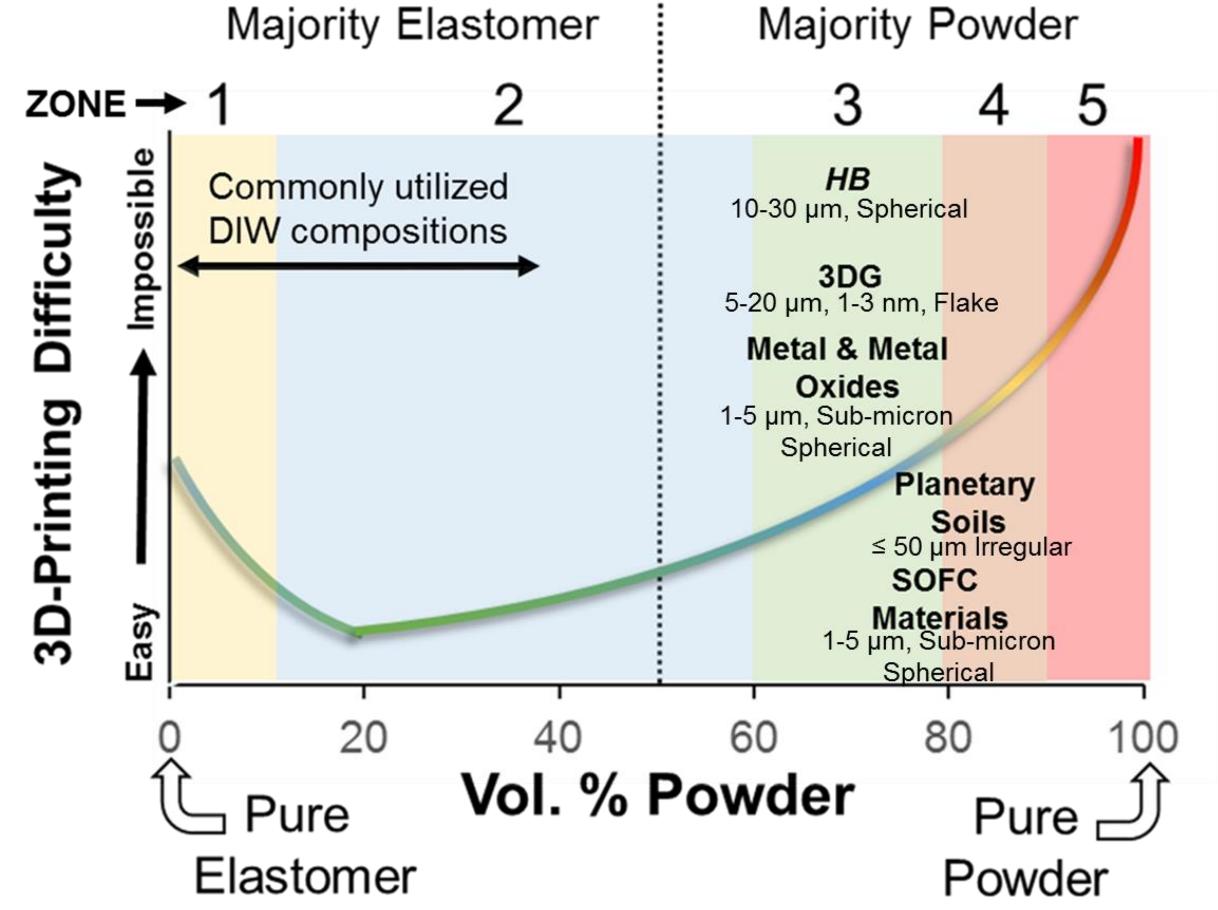




* Maximum speed of the hardware we are utilizing. Not material limited.
** Maximum diameter tested

Standard DIW and Composite Filament FDM

TEAM Particle-Laden Inks



3D-Paints

3D-Paints are composed primarily of the functional particle/powder rather than of non-functional polymer

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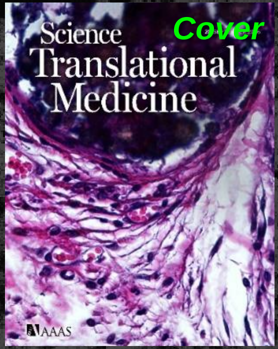
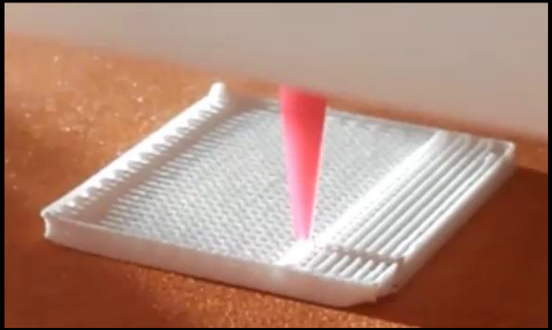
Hyperelastic “Bone”

Hyperelastic "Bone": A Highly Versatile, Growth Factor–Free, Osteoregenerative, Scalable, and Surgically Friendly Biomaterial



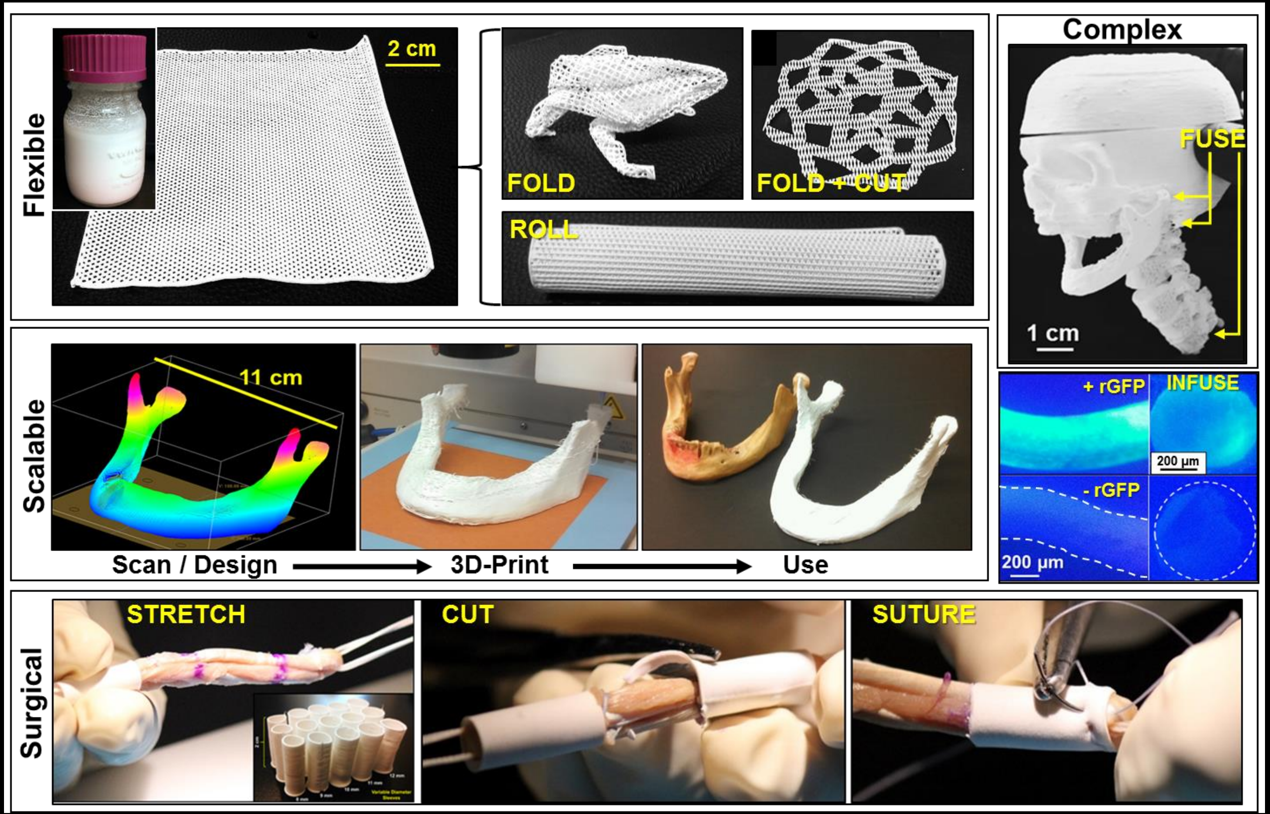
A. E. Jakus, R. N. Shah, *et al*. *Science Translational Medicine* **8**(358), 2016.

Hyperelastic Bone – A New Class of Biomaterials



90-95 wt.% Hydroxyapatite
(High Bioactivity)

Remains highly elastic
(Surgically Friendly)

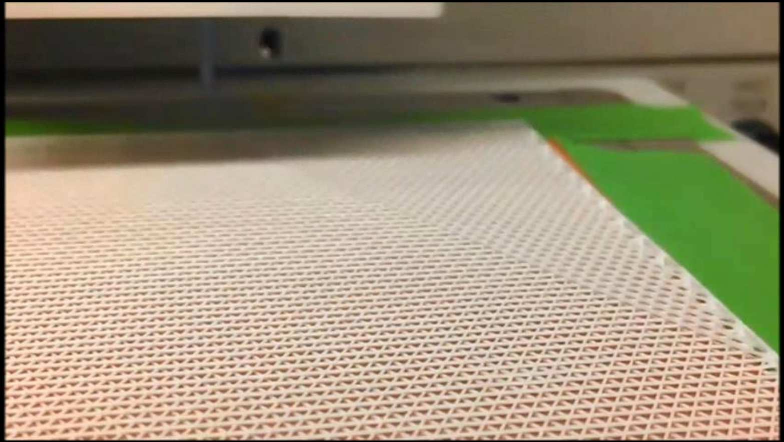


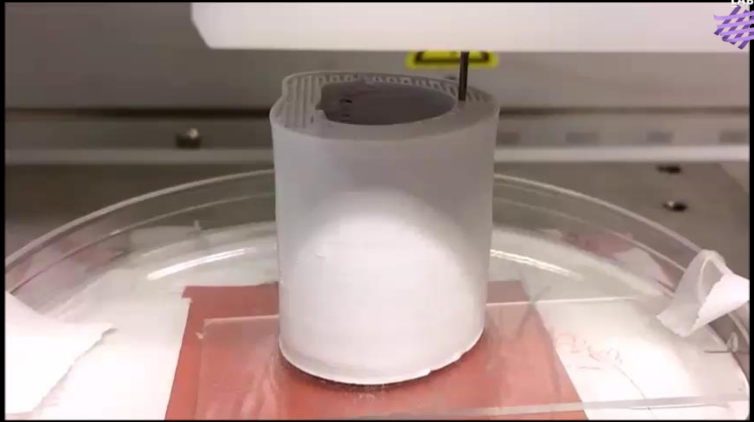
No need for post-processing other than washing and sterilization

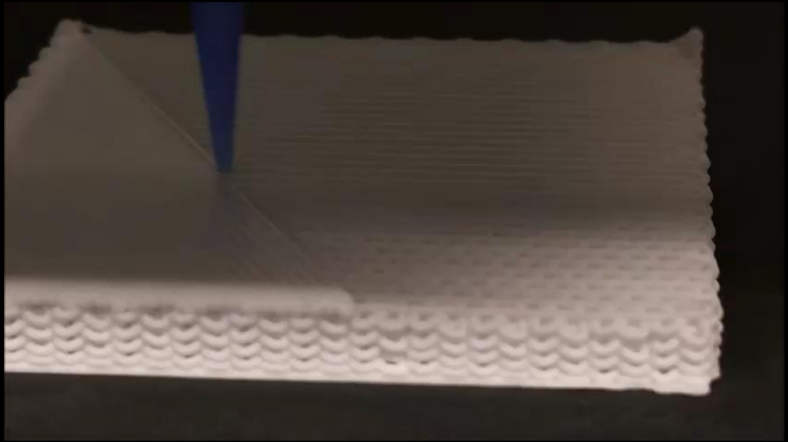
ROLL

90-95 wt.% Hydroxyapatite (High Bioactivity)
Yet Flexible

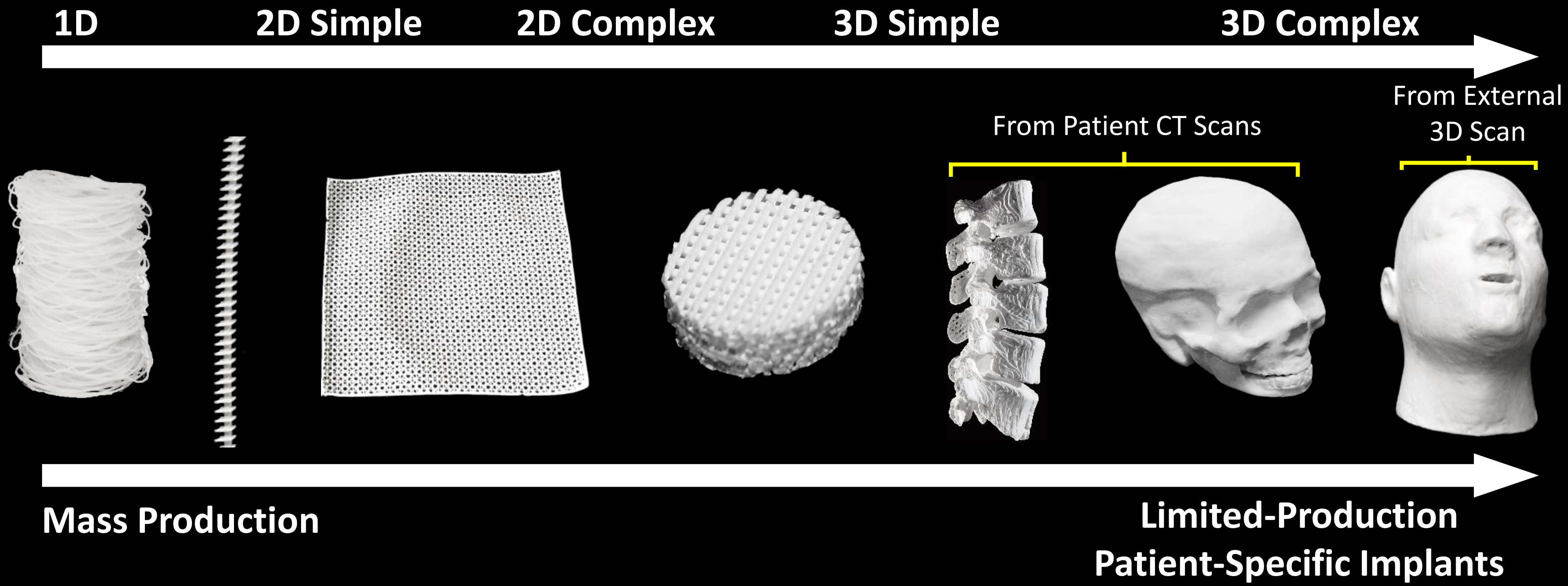
SHAH TEAM LAB







3D-Printing: It's no longer just for anatomy matched implants



New processes are leading to fabrication rates 10-100x faster than existing additive (or even subtractive) manufacturing processes

Note: Objects not shown to scale

AE Jakus and RN Shah et al. *Science Translational Medicine*. 8(358), 2016.

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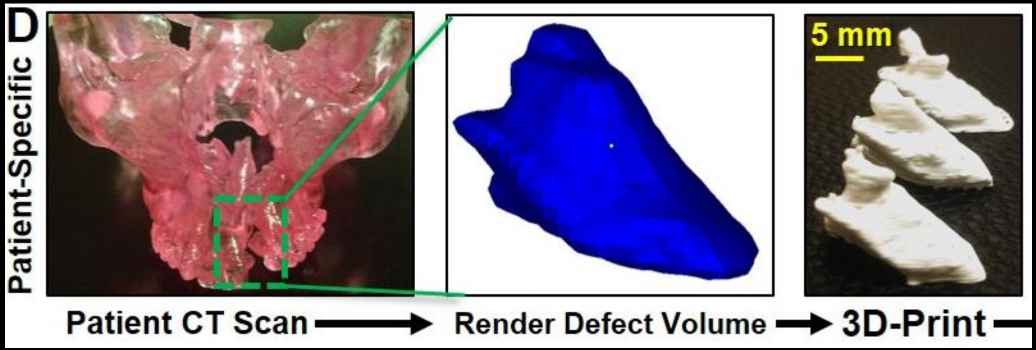
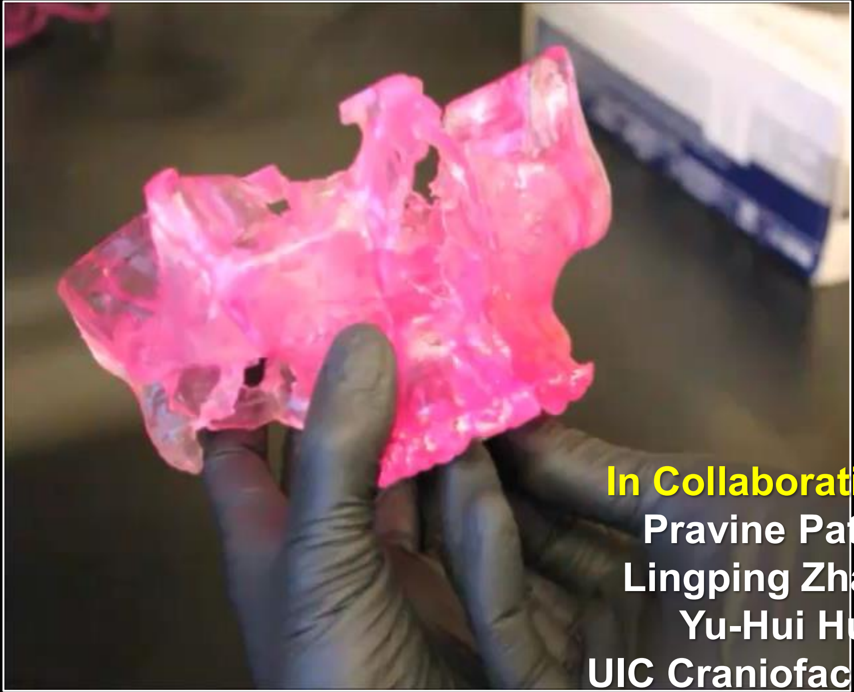
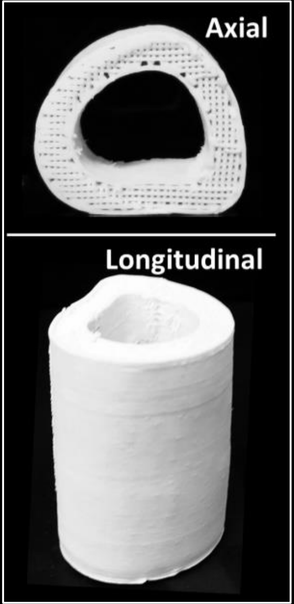
Mechanical Properties

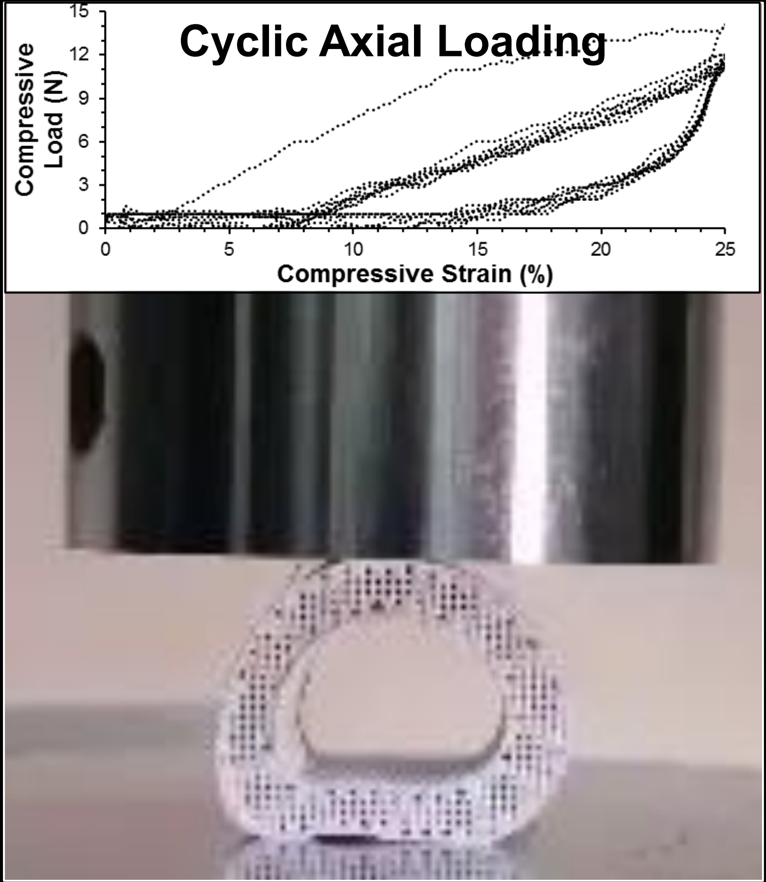




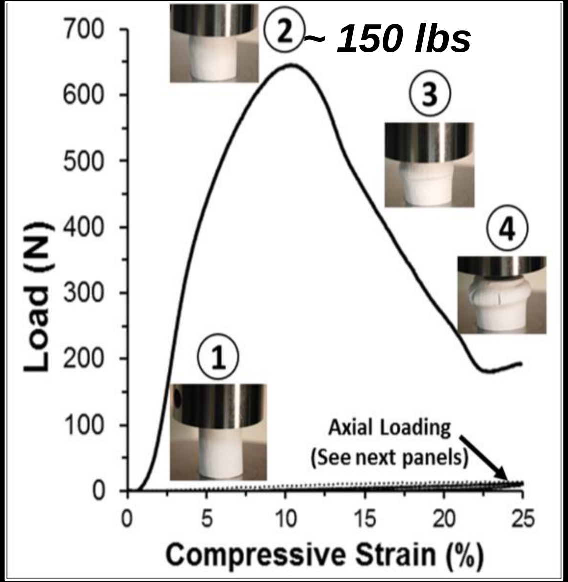
In Collaboration with:
Pravine Patel, MD
Lingping Zhao, PhD
Yu-Hui Huang
UIC Craniofacial Center

Load Bearing Capacity of HB



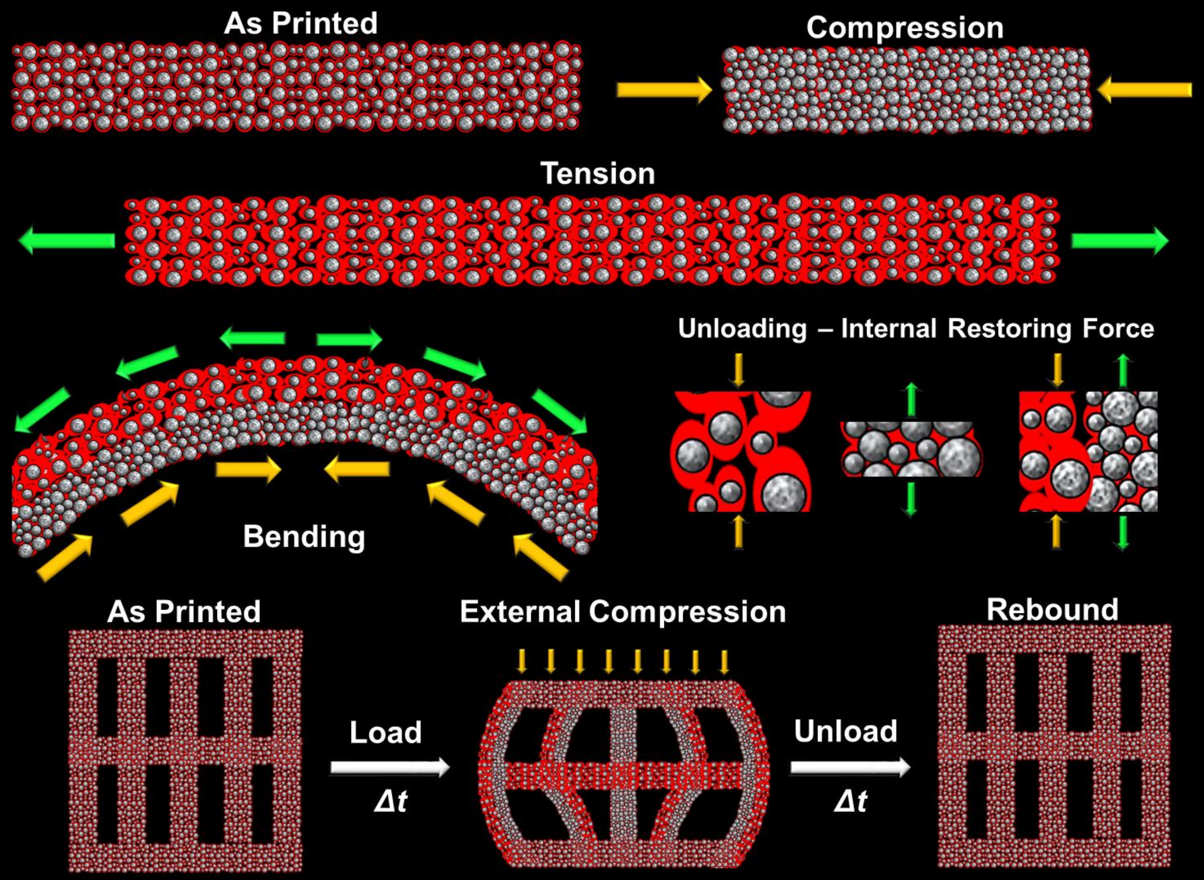


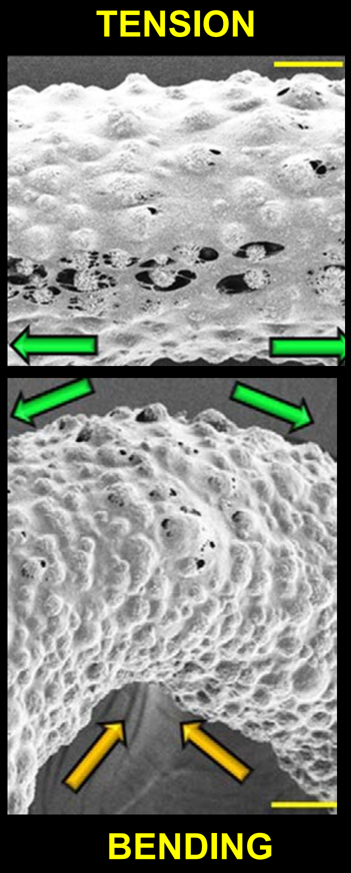
Longitudinal Loading



Max. Load = 650 N (150 lbs)

MECHANICAL PROPERTIES: THE MECHANISM





Elastomer carries the mechanical Loads ("Like rocks joined by rubber bands")

HB v. Common Polymer-CaP Composites: *Microstructural and Mechanical Property Differences*

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HOT-MELT FDM 3D-PRINTED
(1:4 Ceramic:Polymer by volume)

Surface dominated by polymer
(HA bioactivity is shielded)

50 wt.% Ceramic

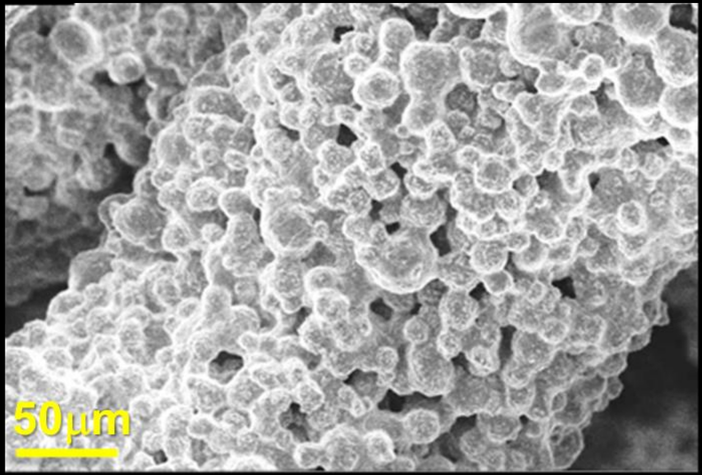
ROOM TEMP <u>HYPERELASTIC BONE</u>
(4:1 Ceramic:Polymer by volume)

Surface dominated by HA particles
(Biologically Beneficial)

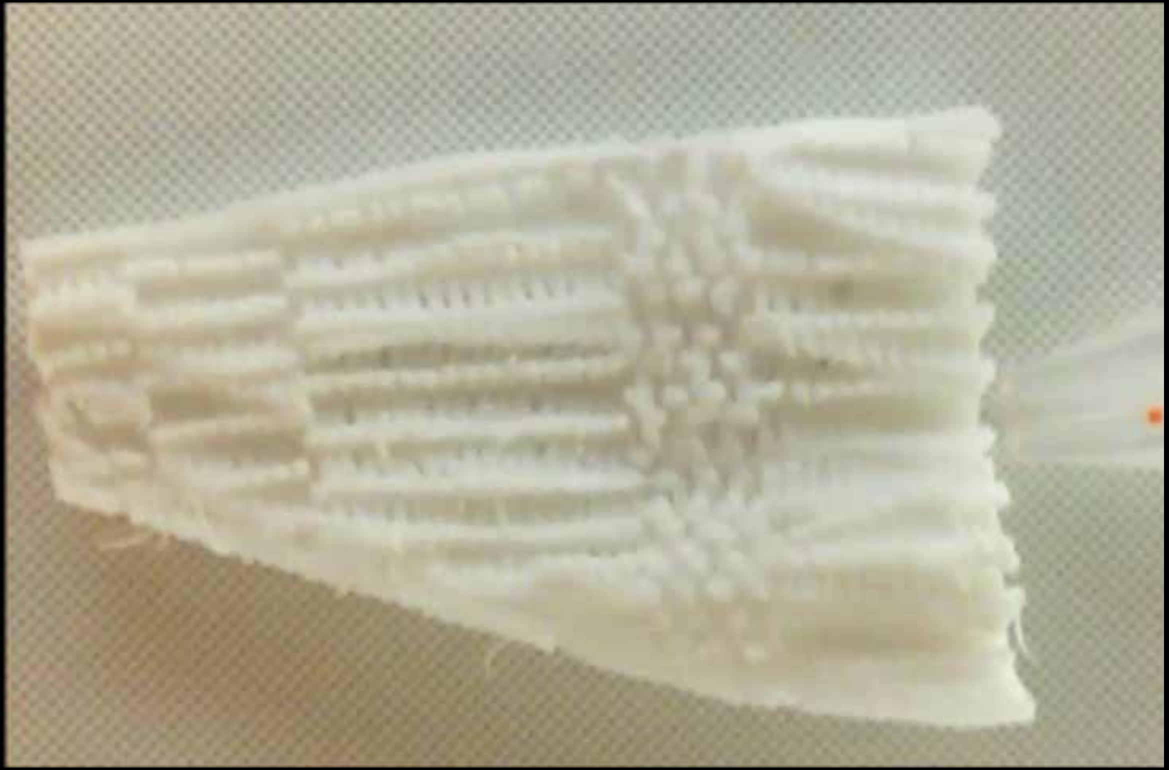
90 wt.% Ceramic

Exact same polymer, exact same ceramic

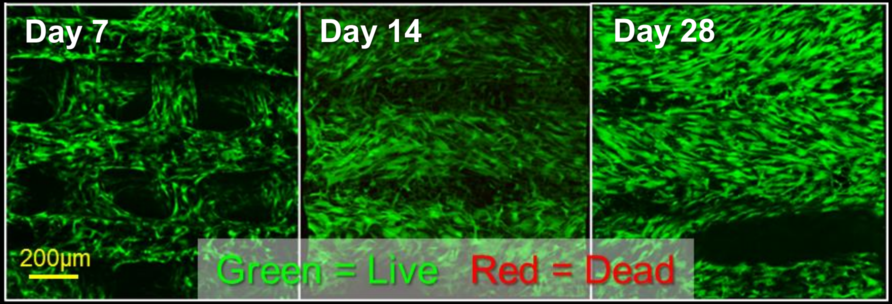
HB: Microstructural & Absorption Properties



HB is ~50% porous
(material porosity)

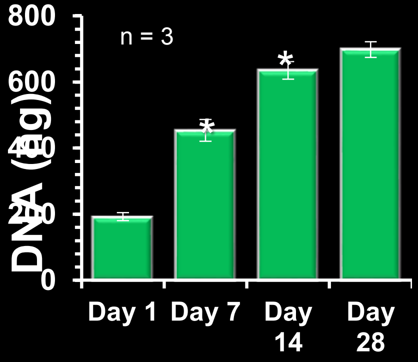


hMSC Proliferation and Osteogenic Differentiation



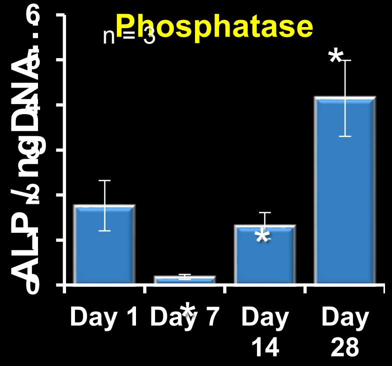
Female human mesenchymal stem cells are viable

hMSCs Proliferate

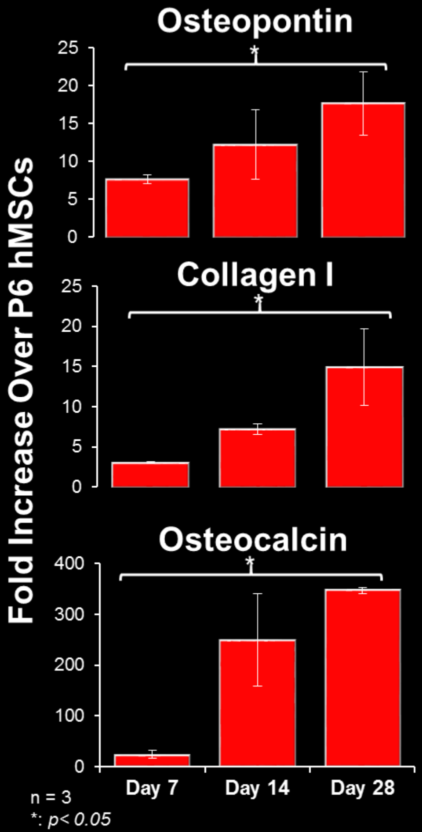


*: p ≤ 0.05 over previous time point

hMSCs Express Alkaline Phosphatase



*: p ≤ 0.05 over previous time point



Upregulation of osteogenic-relevant genes

Note: This was all performed in simple DMEM media without osteogenic factors

IN VIVO: BIOCOMPATIBLIITY → MOUSE

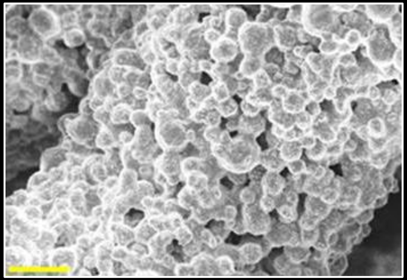
Hyperelastic Bone

90 wt% HAp

Room-Temp. Printed From Liquid Ink

Hyperelastic Mech. Properties

50% Porous



Days 7 & 35
n = 3

BALB/c
Subcutaneous Implants

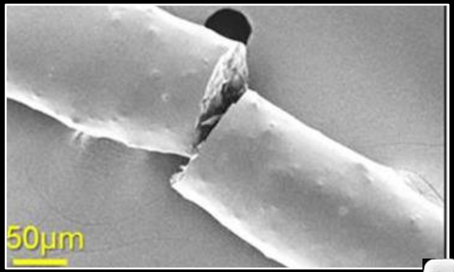
Standard

50 wt% HAp

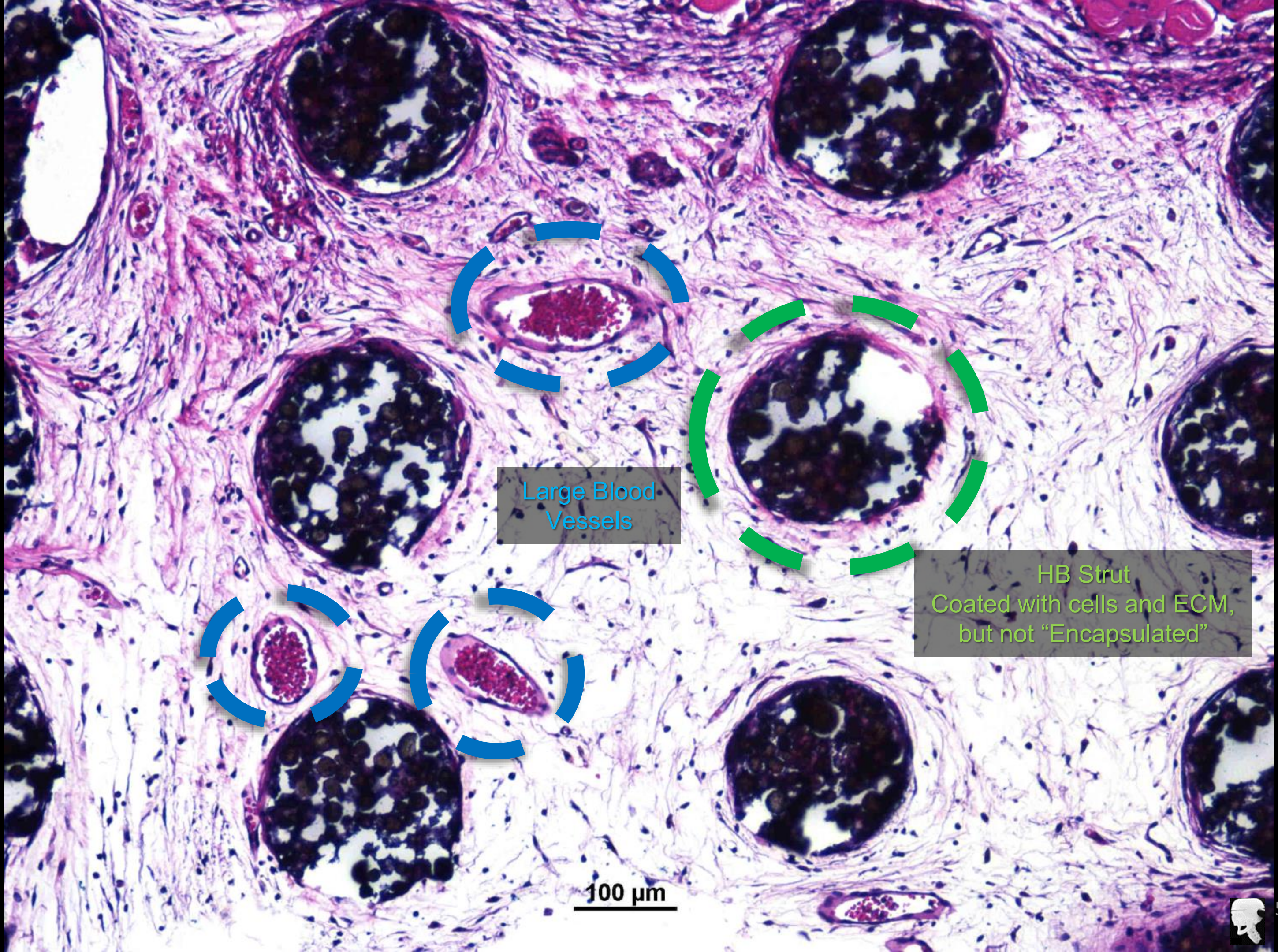
Hot-Melt Printed From Powder Mixture

Very Brittle

Near Fully Dense

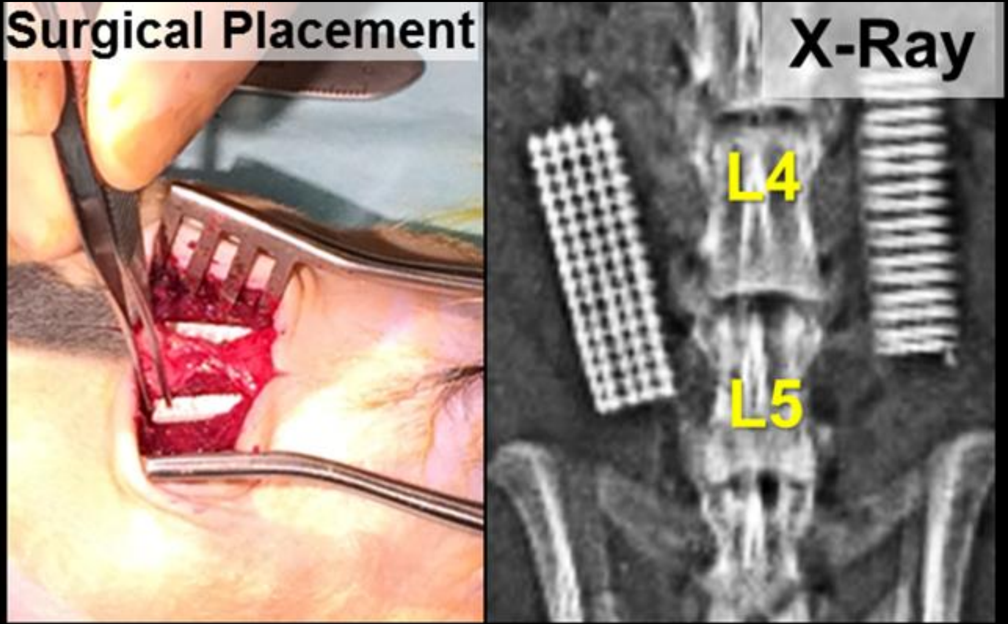


Day 35 H&E


Large Blood Vessels
HB Strut
Coated with cells and ECM, but not "Encapsulated"
100 µm

IN VIVO: SPINAL FUSION → RAT

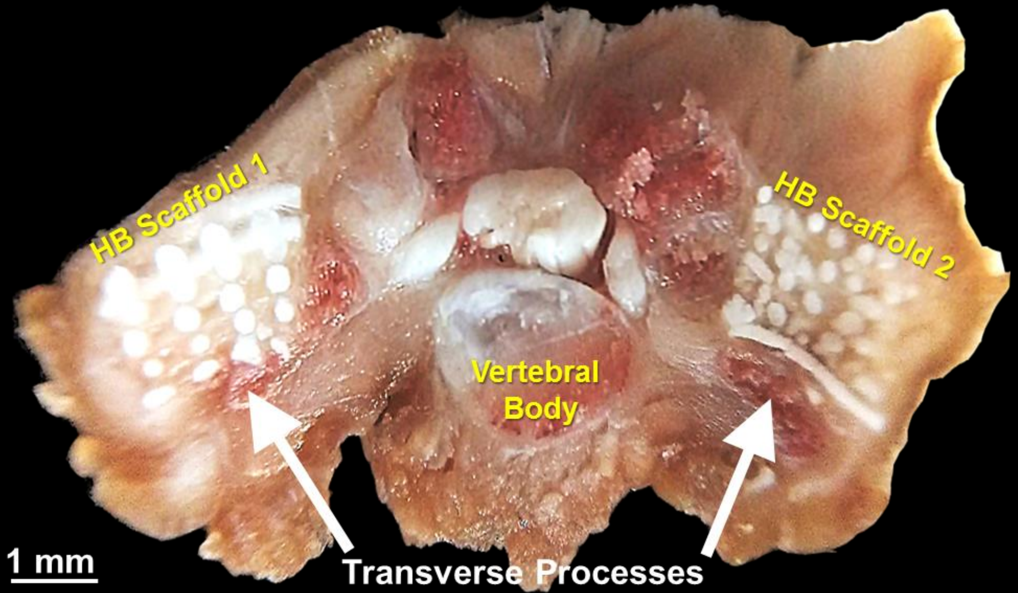
Male Sprague Dawley Rat

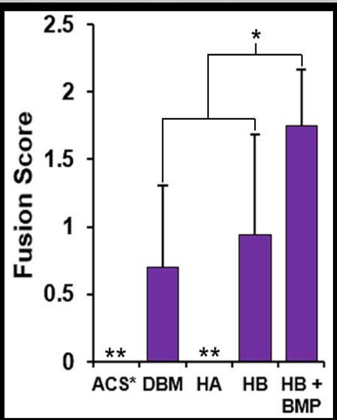


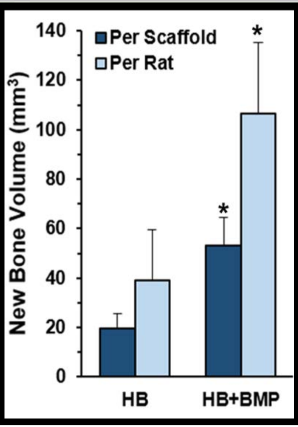
Posterlateral Placement

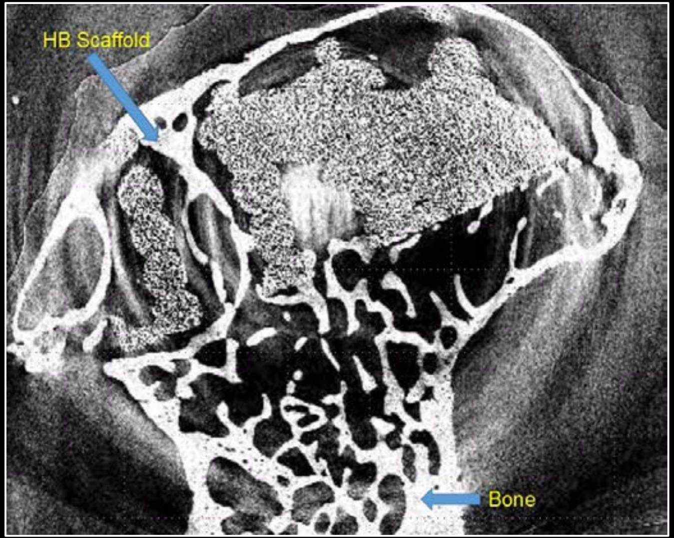
HB (+BMP) HB (-BMP)

HB in Rat Spinal Fusion Model









Hyperelastic Bone is as effective as demineralized bone matrix
And can potentially serve as an effective carrier for growth factors

Collaboration with Erin & Wellington Hsu (Orthopedic Surgery) and Stuart Stock

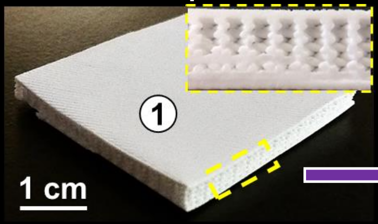
IN VIVO: FULL-THICKNESS CRANIAL DEFECT → LARGE PRIMATE

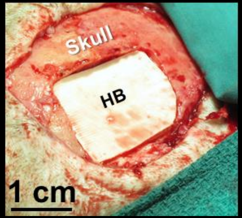
In collaboration with Prof. Lee Miller and Group (NU)

Rhesus macaque

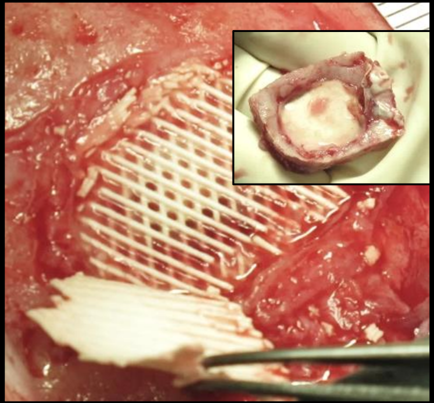
HB in Large Primate Calvarial Defect Case Study

HB Implant

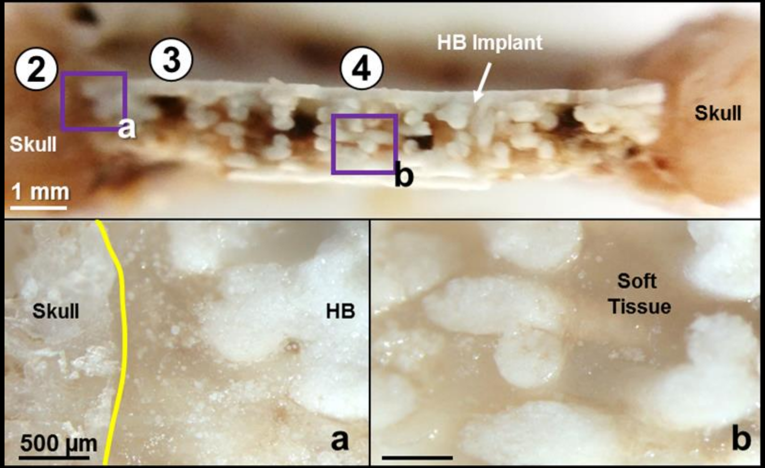


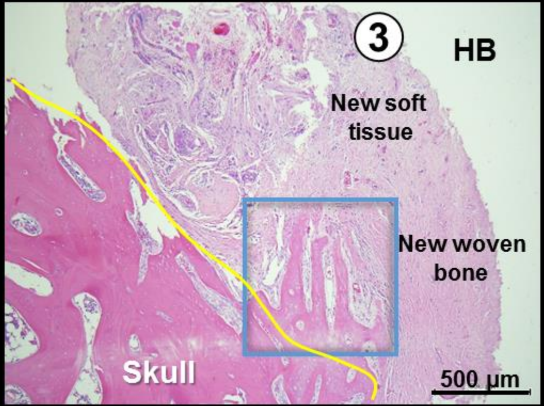


4 Weeks Explant

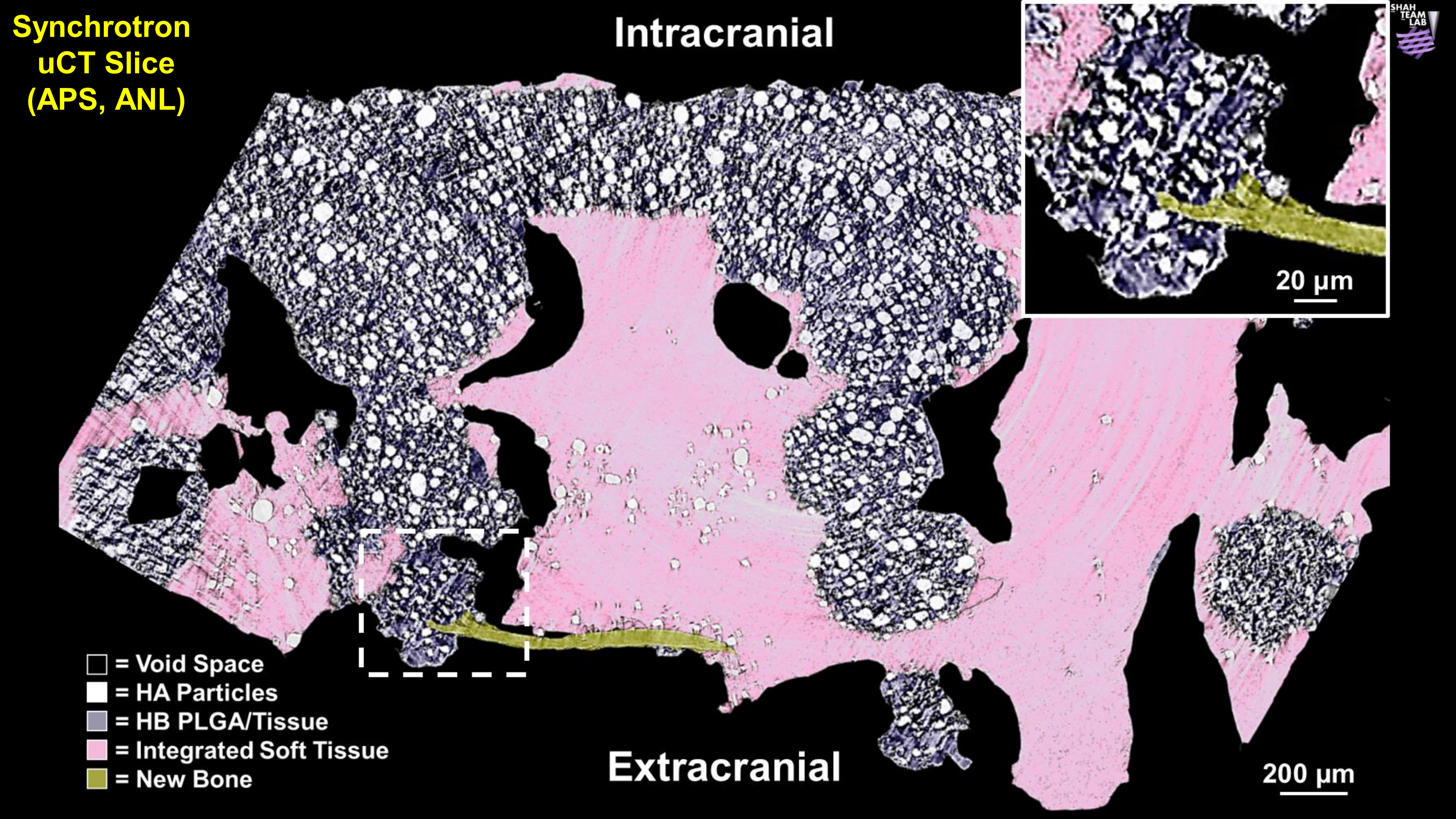


"Easy to shape and press fit into irregular defect site"



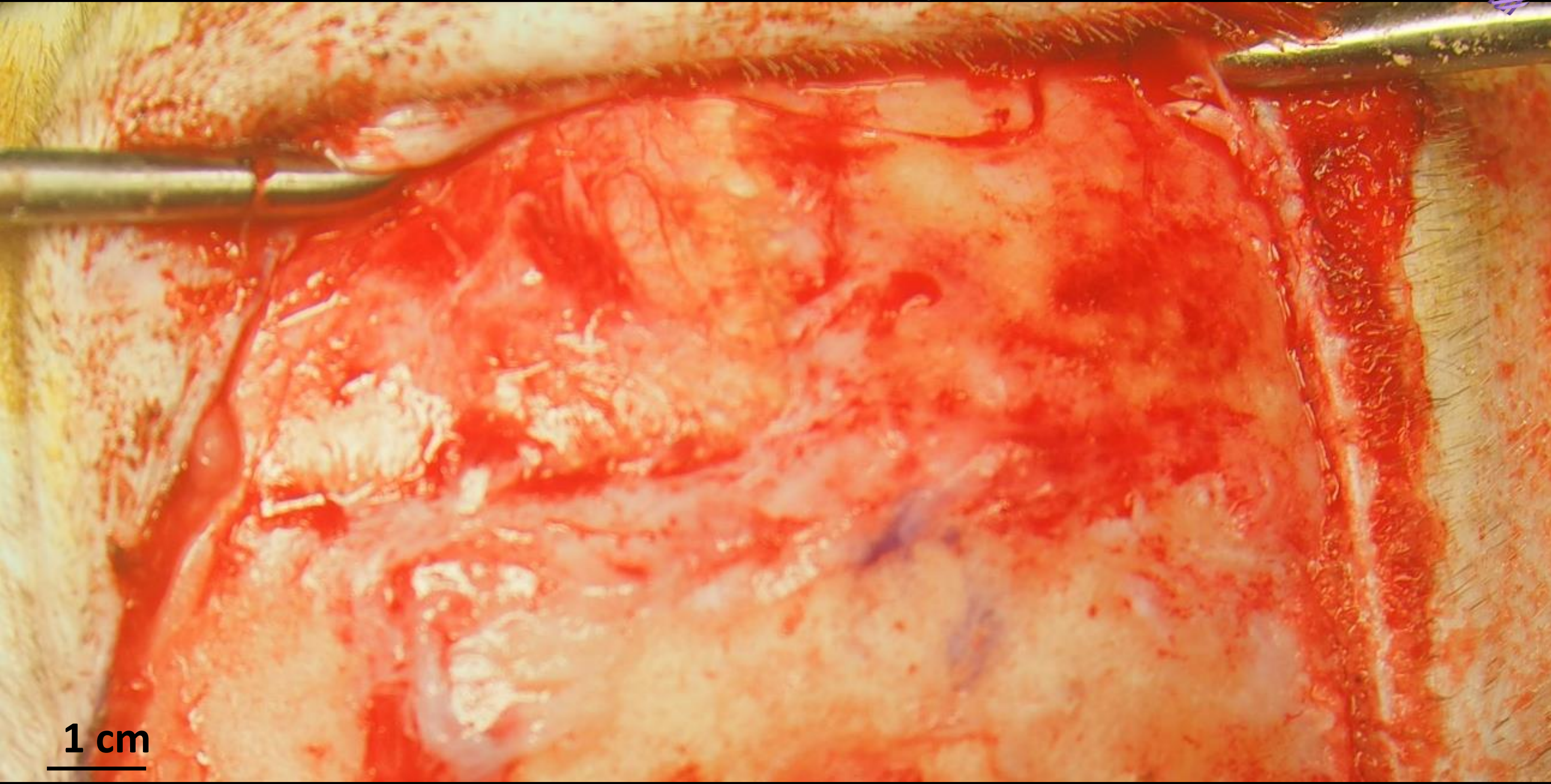


Evidence of new bone formation at Skull-HB interface by 4 weeks

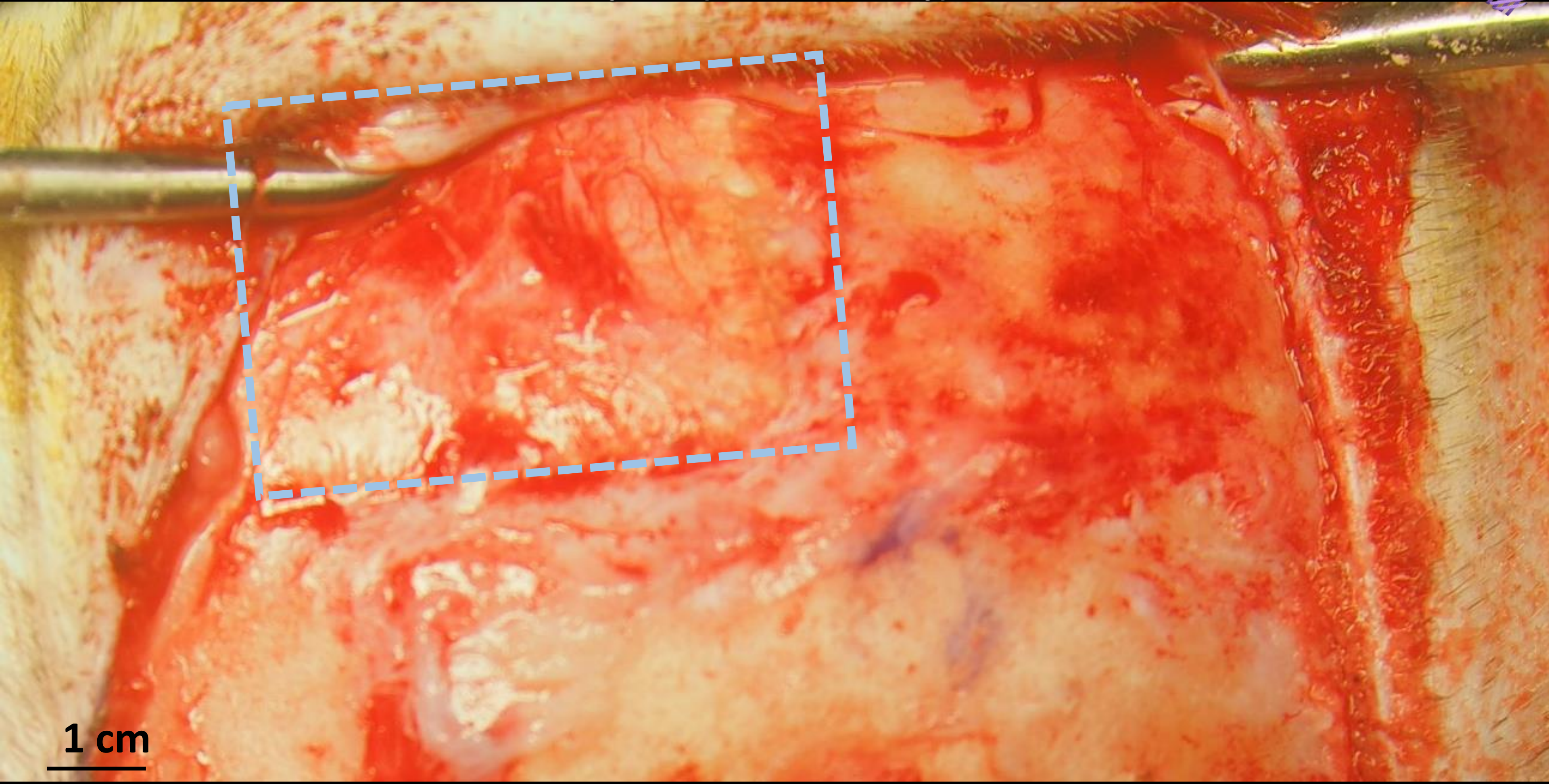


Synchrotron
uCT Slice
(APS, ANL)
Intracranial
Extracranial
20 μm
200 μm
= Void Space
= HA Particles
= HB PLGA/Tissue
= Integrated Soft Tissue
= New Bone
SHAH TEAM LAB

2nd HB Cranial Implant (Same Monkey) after 13 months

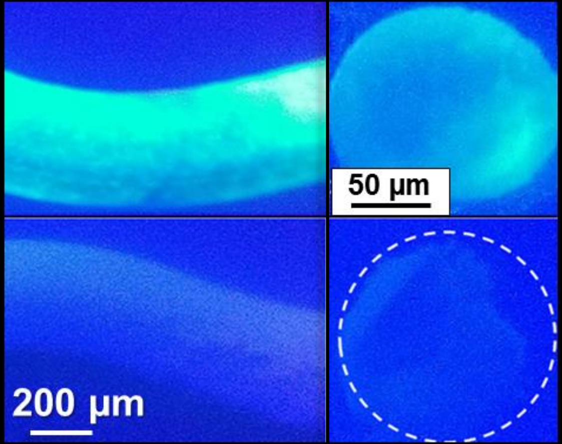


2nd HB Cranial Implant (Same Monkey) after 13 months

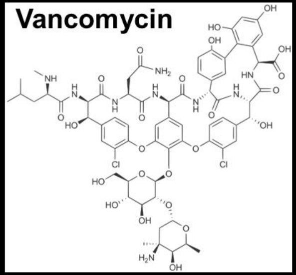


INCORPORATING BIOACTIVE FACTORS, ANTIBIOTICS, ETC.

Room-temperature processing and 3D-printing permits incorporation of bioactive factors that would otherwise be inactivated at elevated temperatures



Extruded HB fiber with (top) and without (bottom) incorporated green fluorescent protein.



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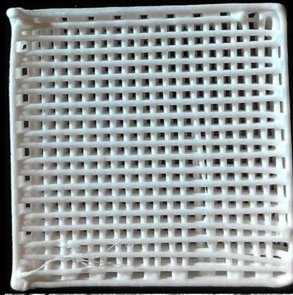
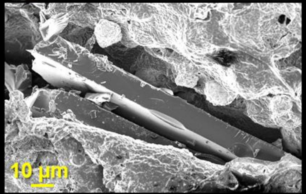
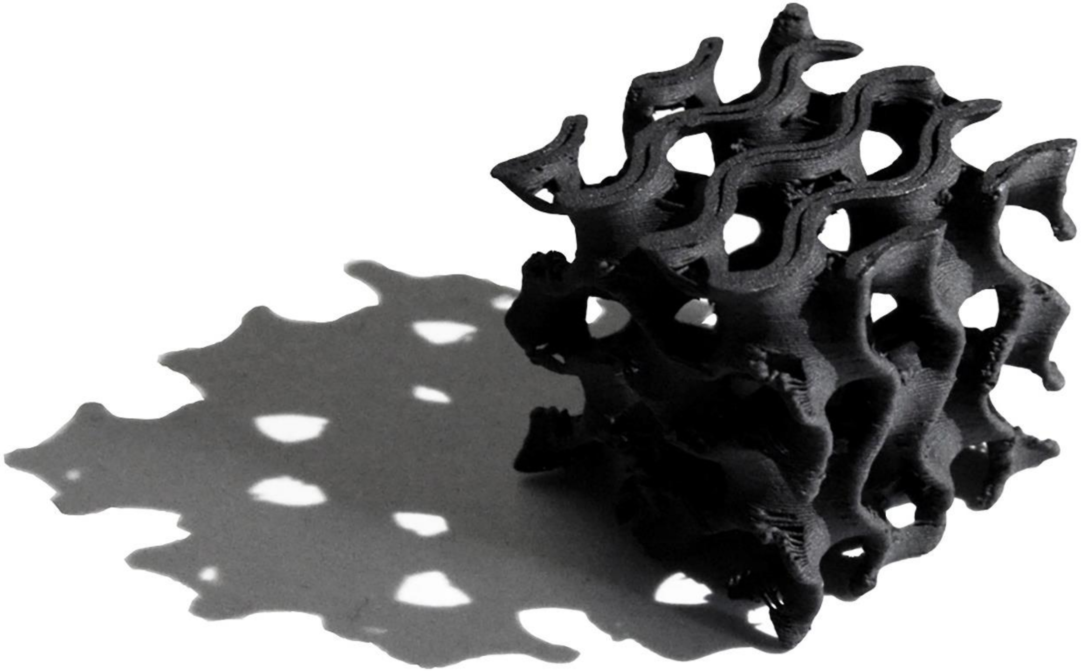




Bioactive factors, antibiotics, and small molecules can be incorporated directly into the inks

3D-Graphene

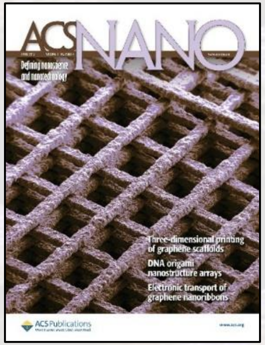


Three-Dimensional Printing of High-Content Graphene Scaffolds for Electronic and Biomedical Applications

808156 ALDRICH

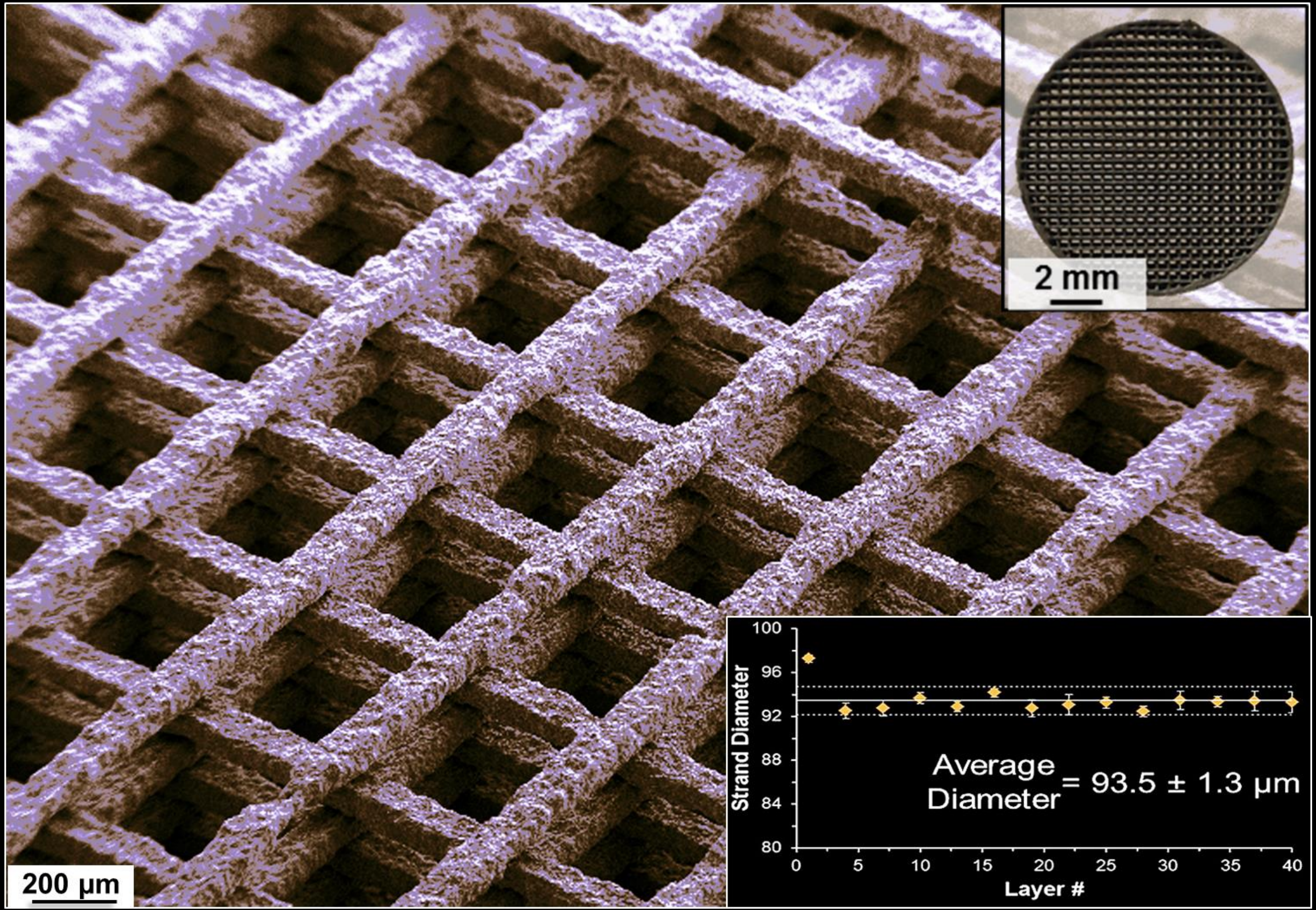
3D Printing Graphene Ink

Currently Available through Millipore Sigma
(Cat.# 808156)



A.E. Jakus, R.N. Shah, *et al*. *ACS Nano* 2015;9(4):4636-4648.
A.E. Jakus & R.N. Shah. *Material Matters*. 11(2). 2016. *Millipore Sigma*.

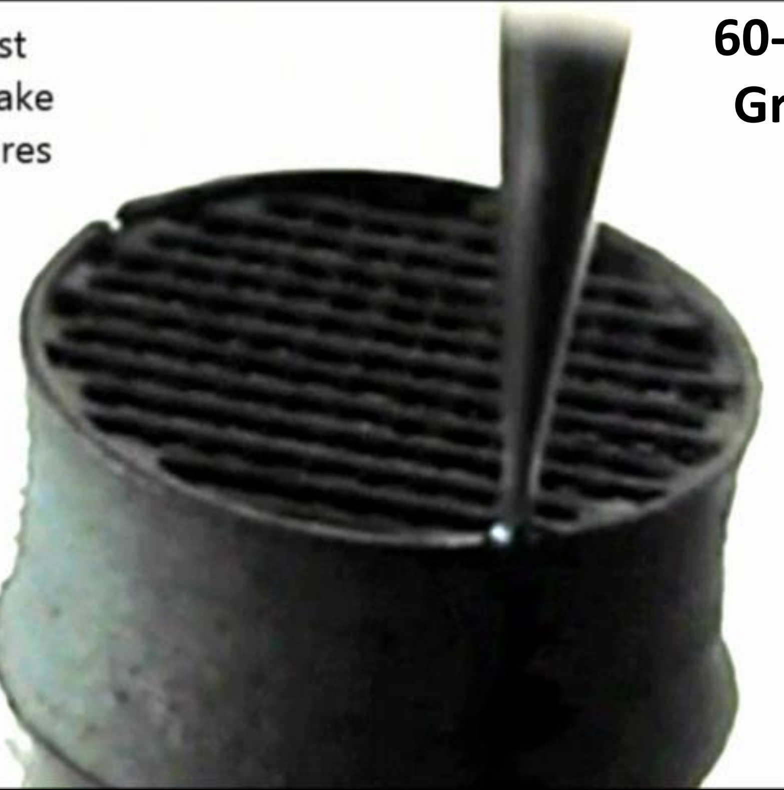
3D-PRINTING CONSISTENCY

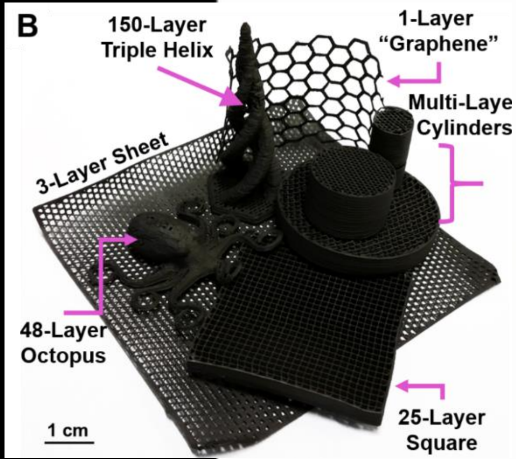


Solid Structures from Liquid 3D-Ink Extrusion

NOTE: Contrast Enhanced to make graphene features visible.

60-70 vol.% Graphene

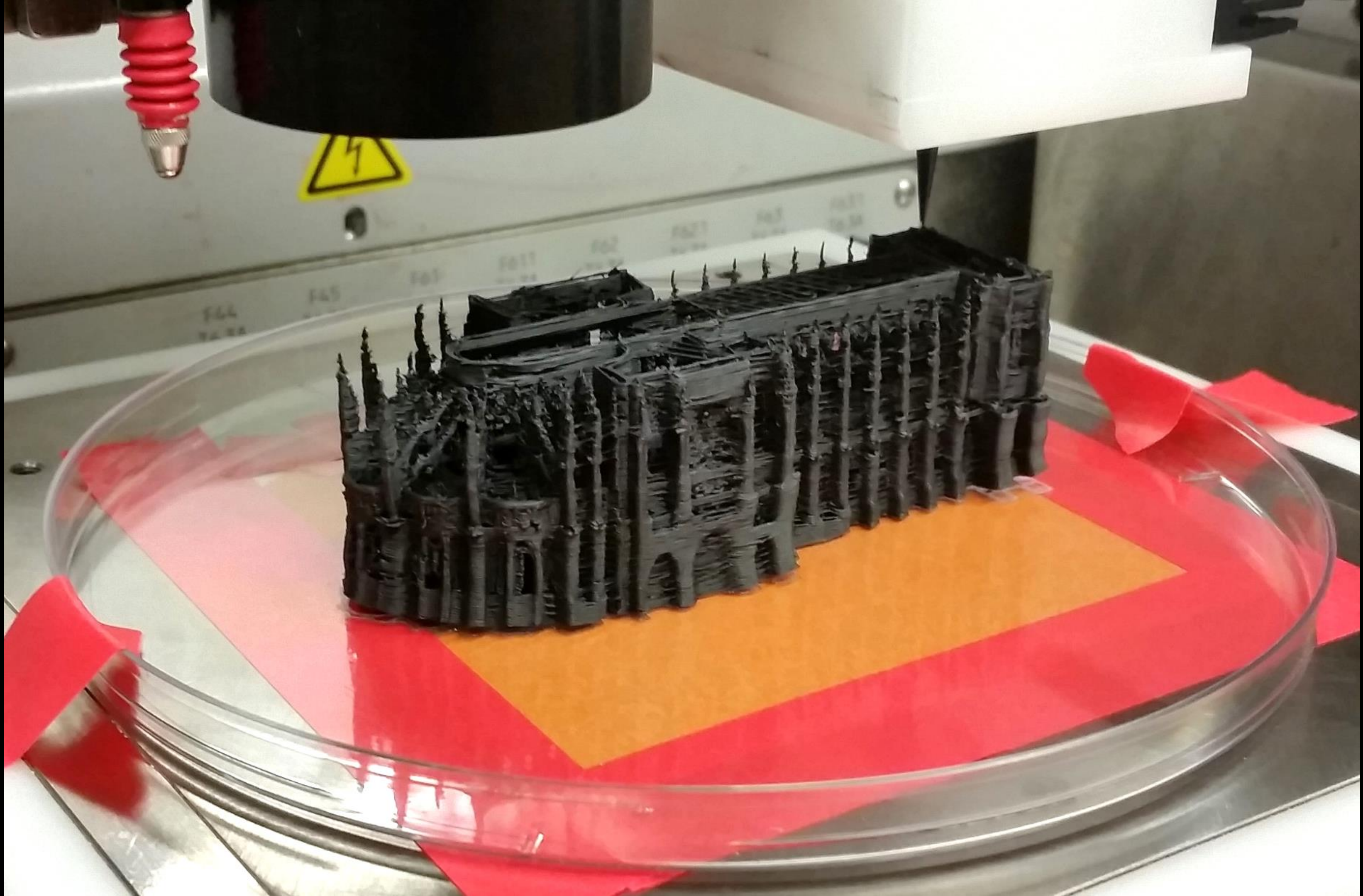




Not a "Graphene enhanced polymer"

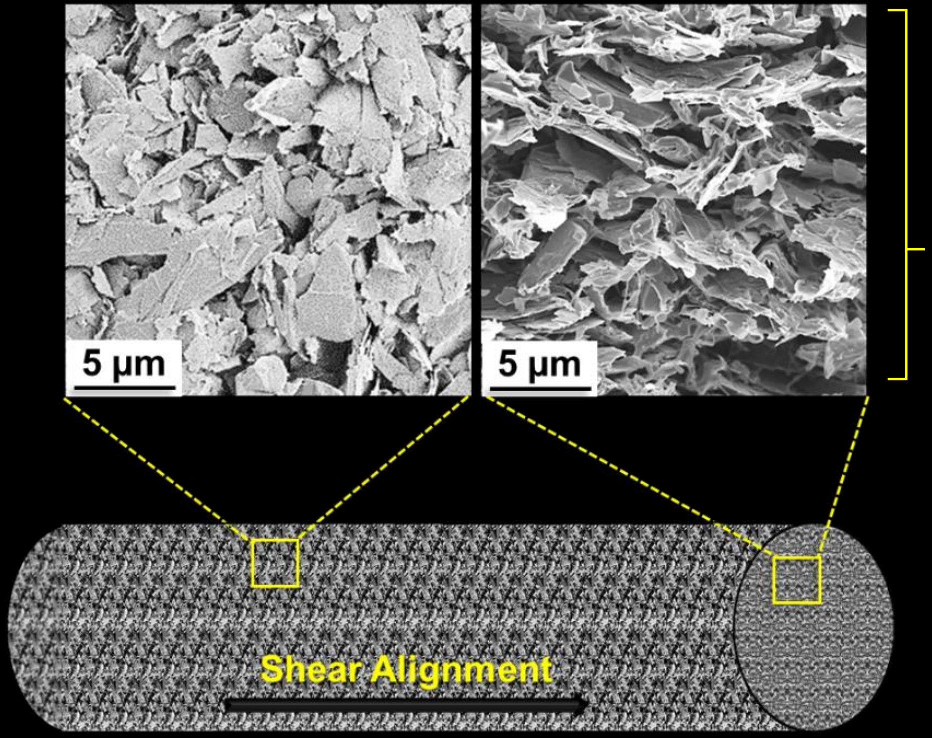
<10 vol.% graphene

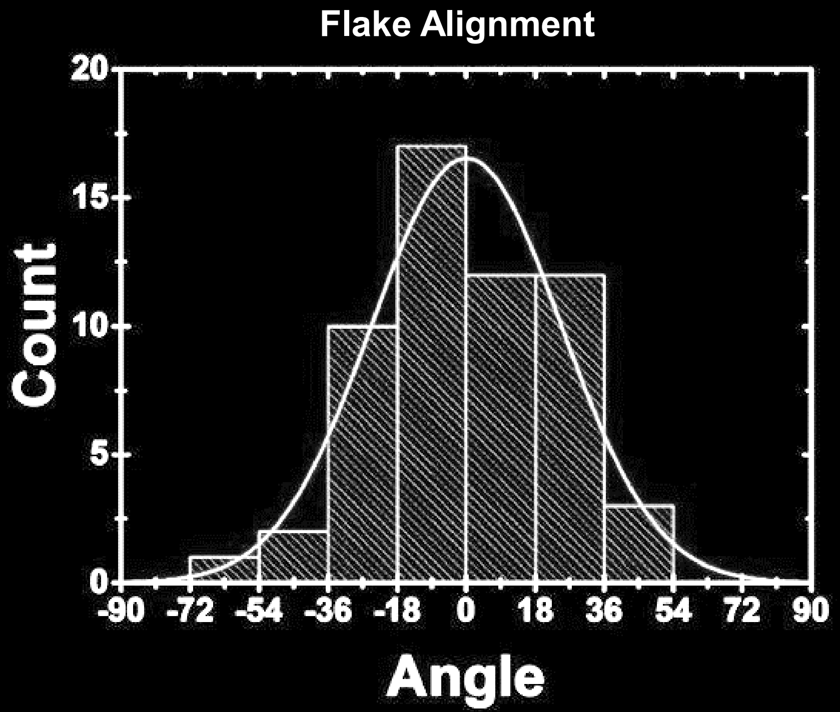
No drying time required before handling objects



SHAH TEAM LAB

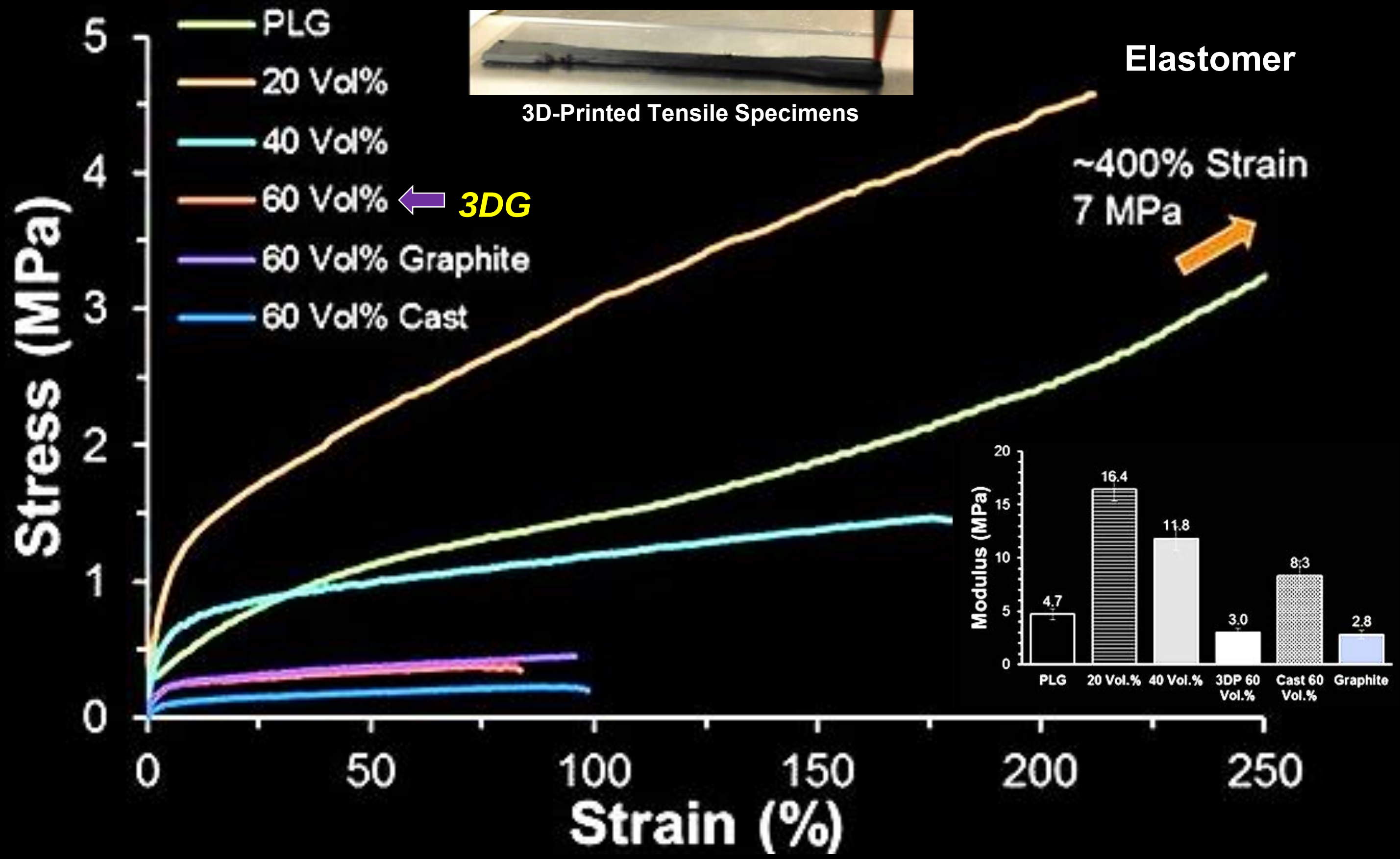
3DG MICROSTRUCTURE AND FLAKE ALIGNMENT



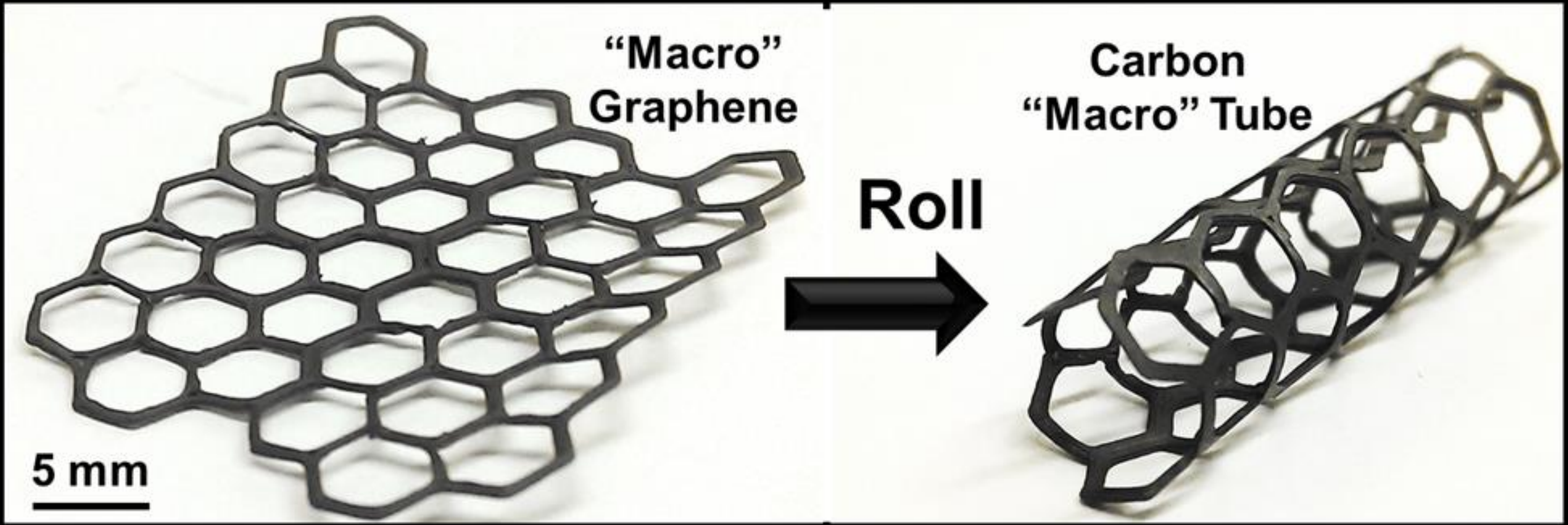


There is a degree of flake alignment along the length of extruded fibers. Graphene flakes are stacked within fiber interiors.

MECHANICAL PROPERTIES: TENSION



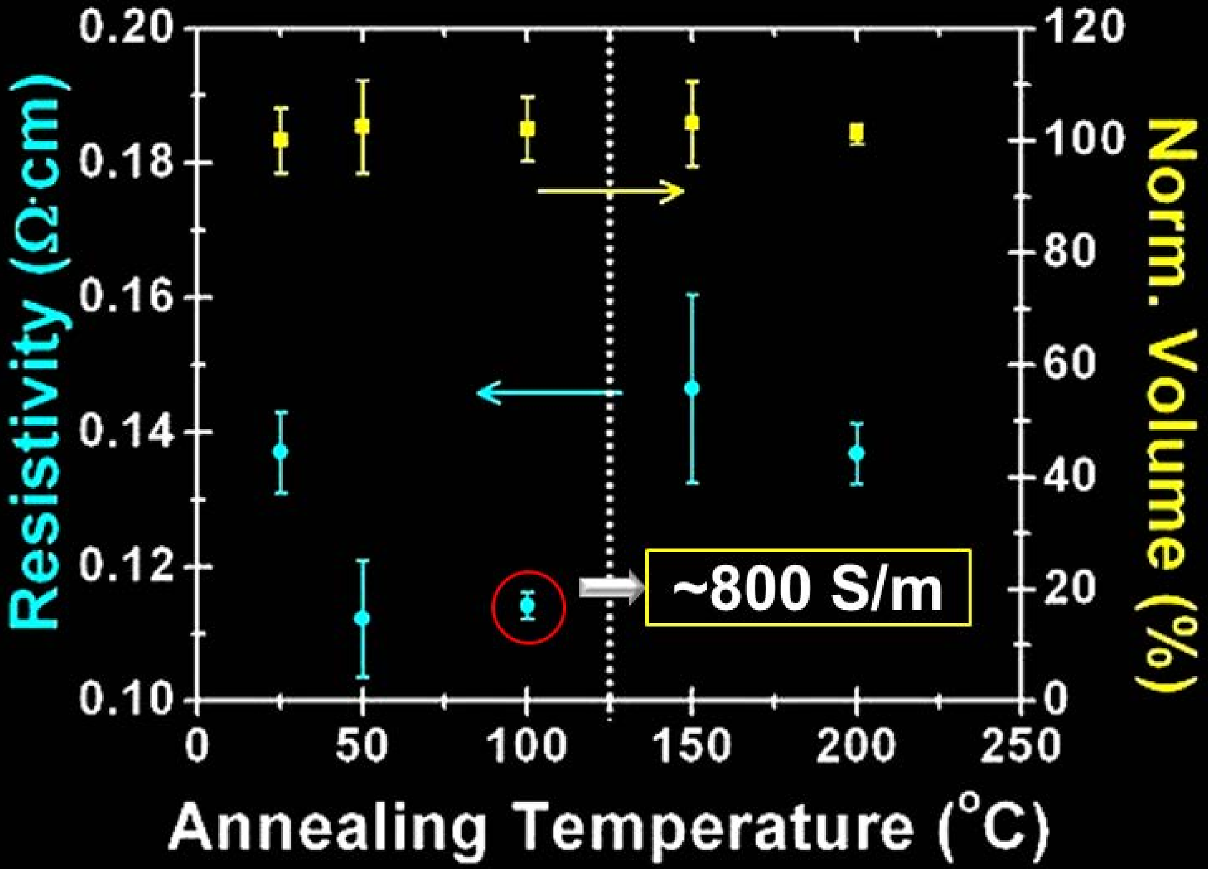
PHYSICAL FLEXIBILITY

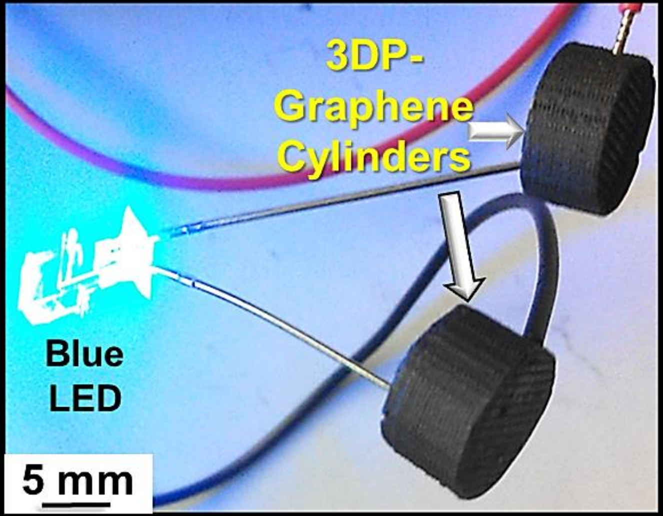


3DG Sheets can be rolled, folded, and cut

This permits architectures that could not be produced directly through 3D-printing to be created.

Electrical Conductivity

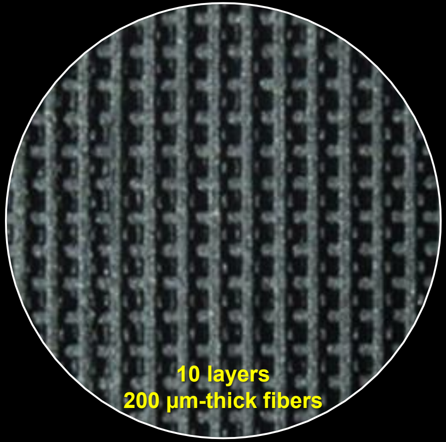


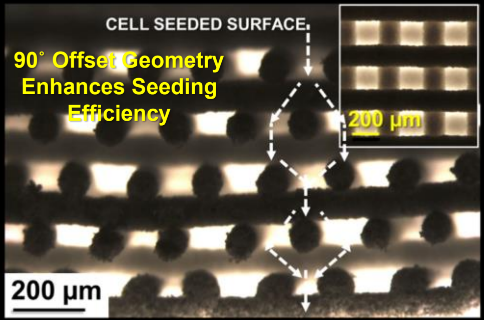


This is the highest recorded conductivity to date for any non-metallic 3D-printed material

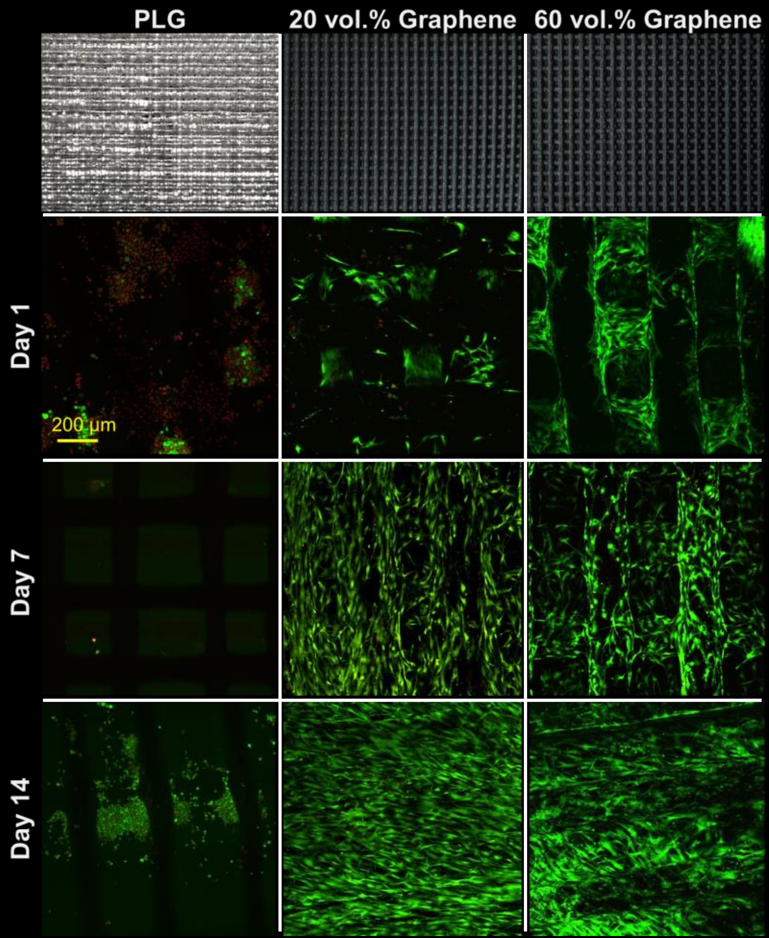
Biocompatibility: *In Vitro*

4 mm-diameter scaffolds punched from larger 3D-printed sheets

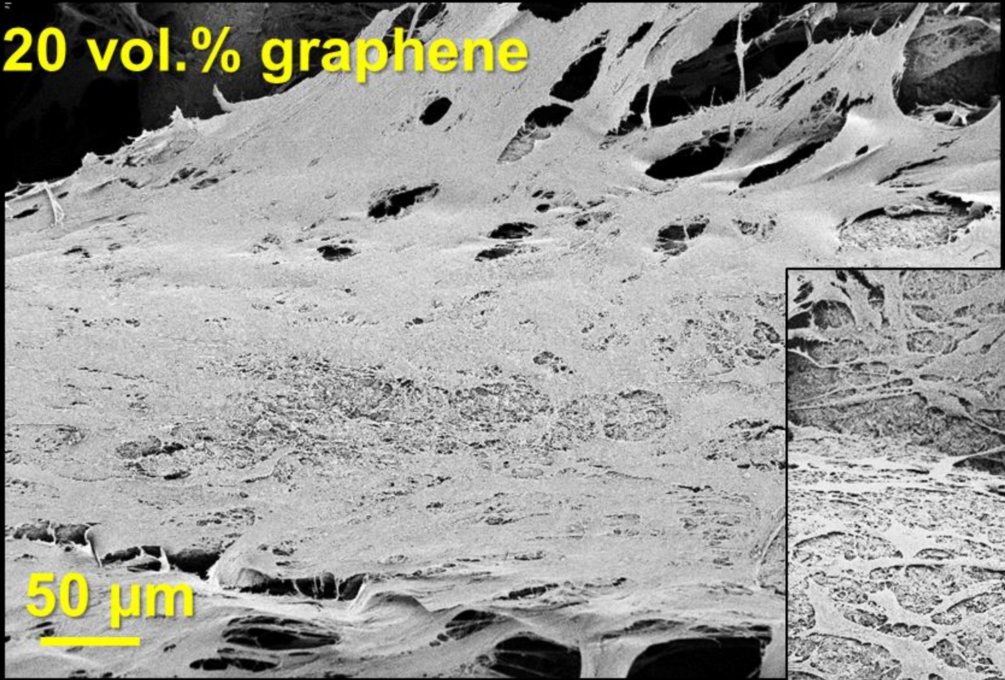


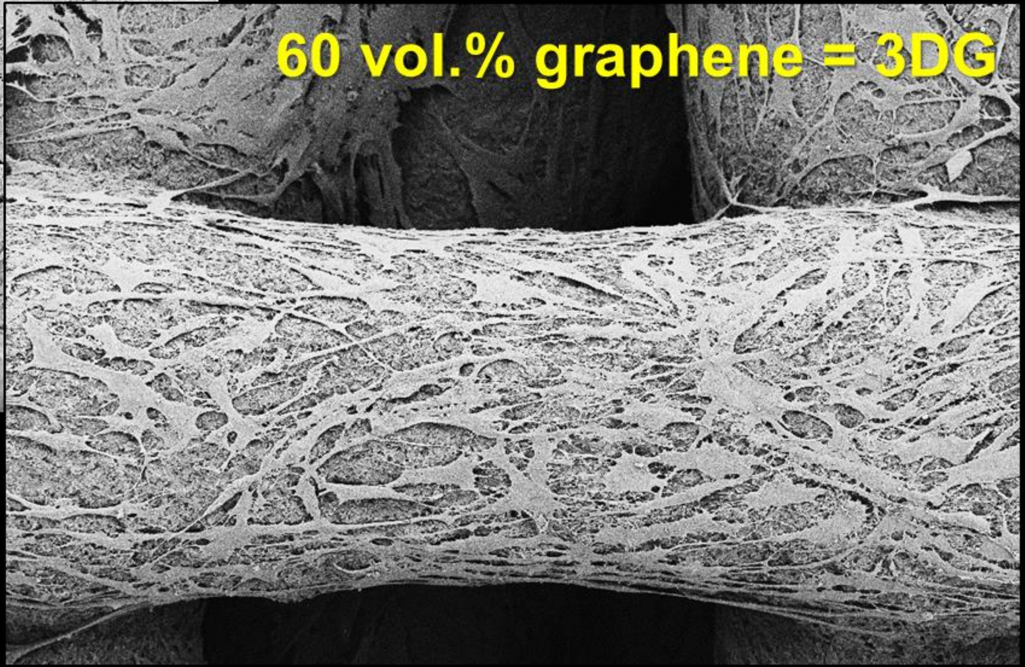


Seeded with 50k human mesenchymal stem cells

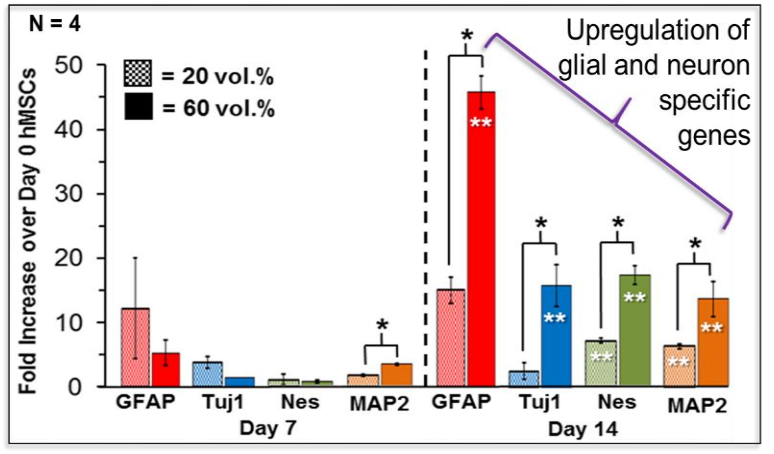


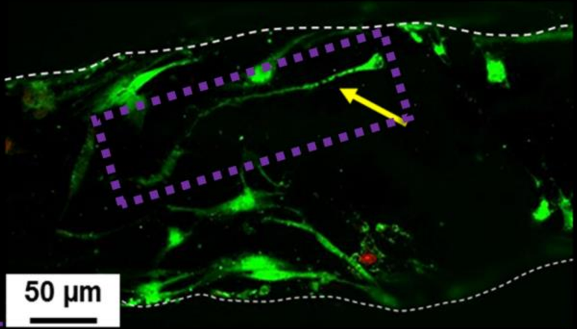
Day 7: Distinct Cell Morphologies

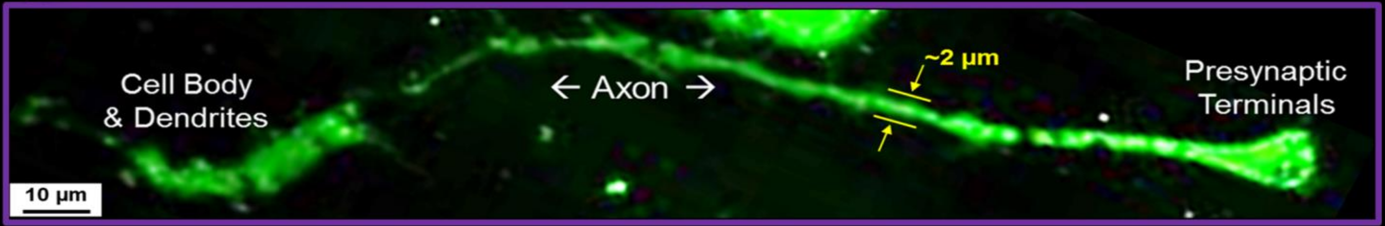




Neurogenic Differentiation



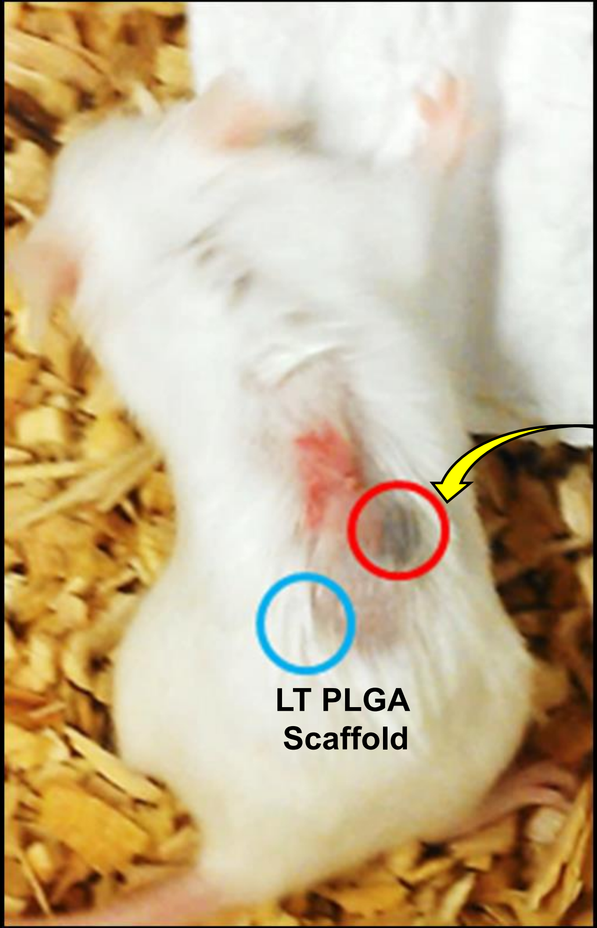


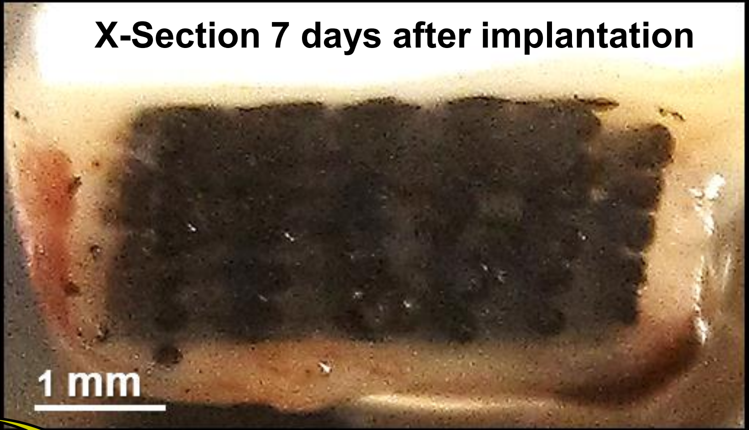


Mesenchymal stem cells in simple basal medium + FBS

No neurogenic factors or stimulus other than material

IN VIVO BIOCOMPATIBILITY STUDIES

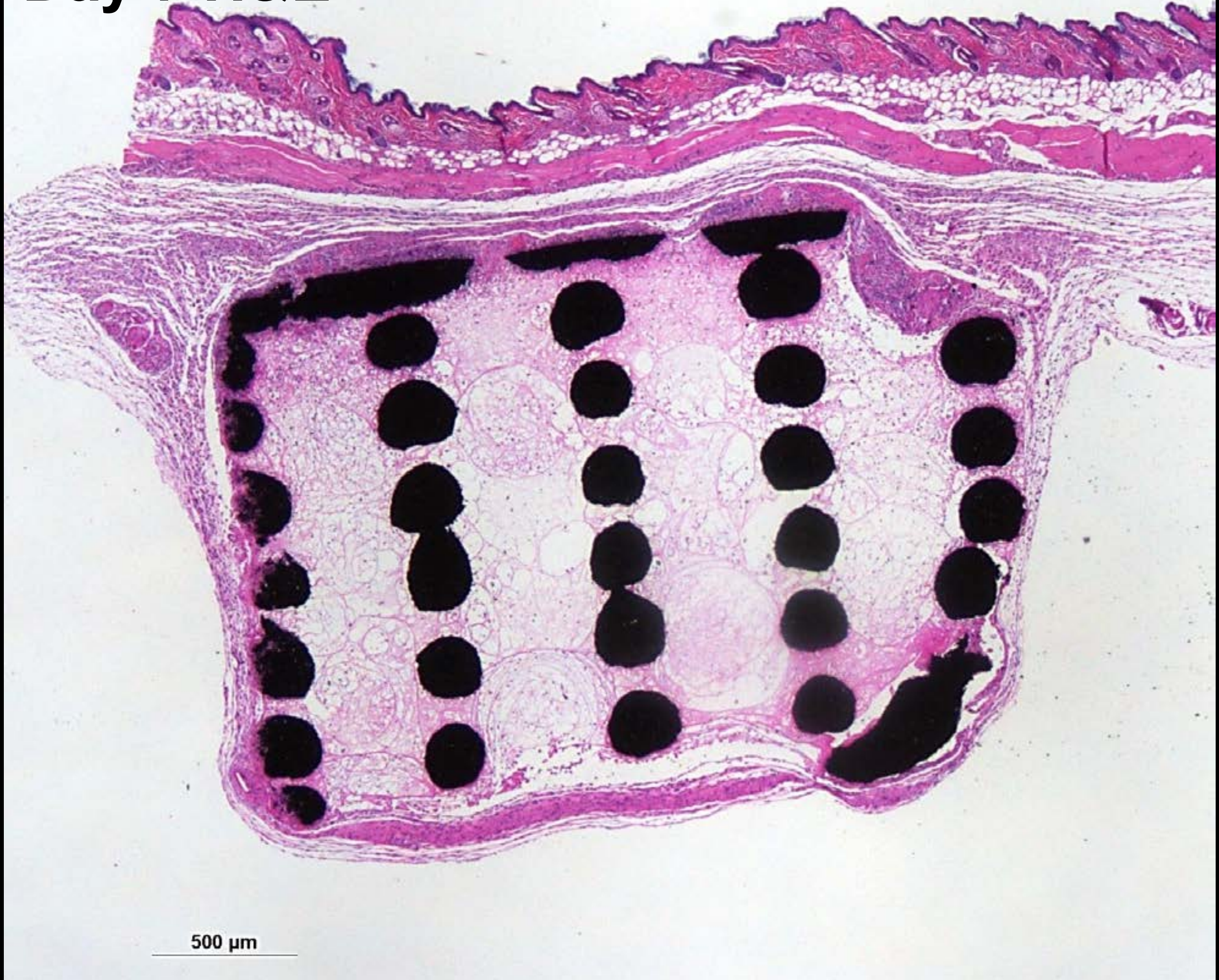




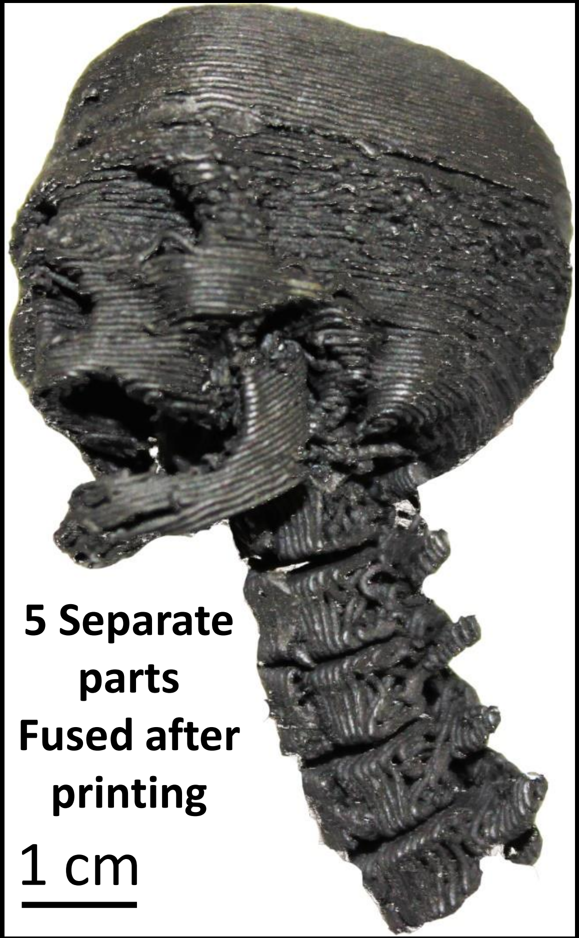
90˚ 3DG and Low-temperature-printed PLGA Scaffolds Subcutaneously Implanted

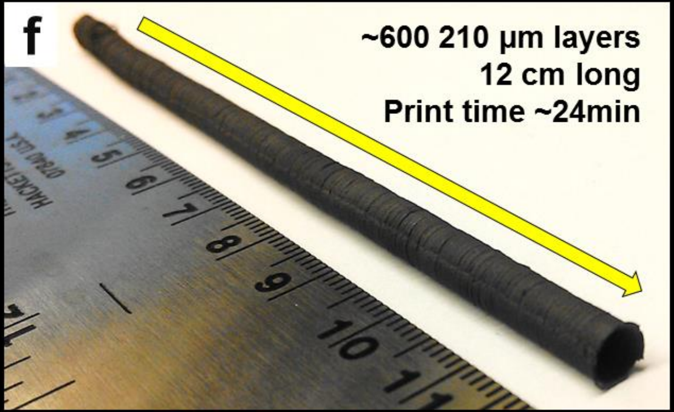
Surgeries performed by Sue Jordan, MD PhD

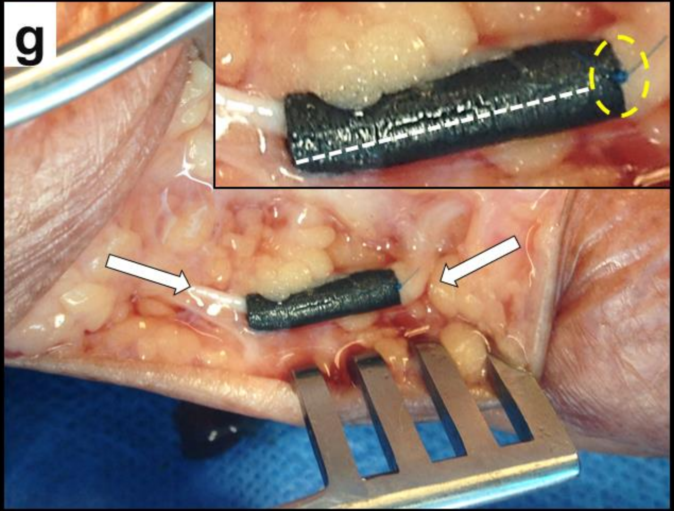
Day 7 H&E



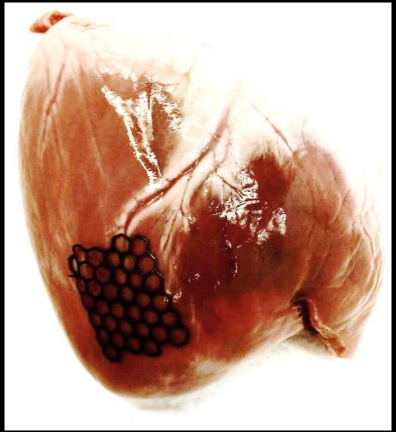
Scalability and Surgical Handling



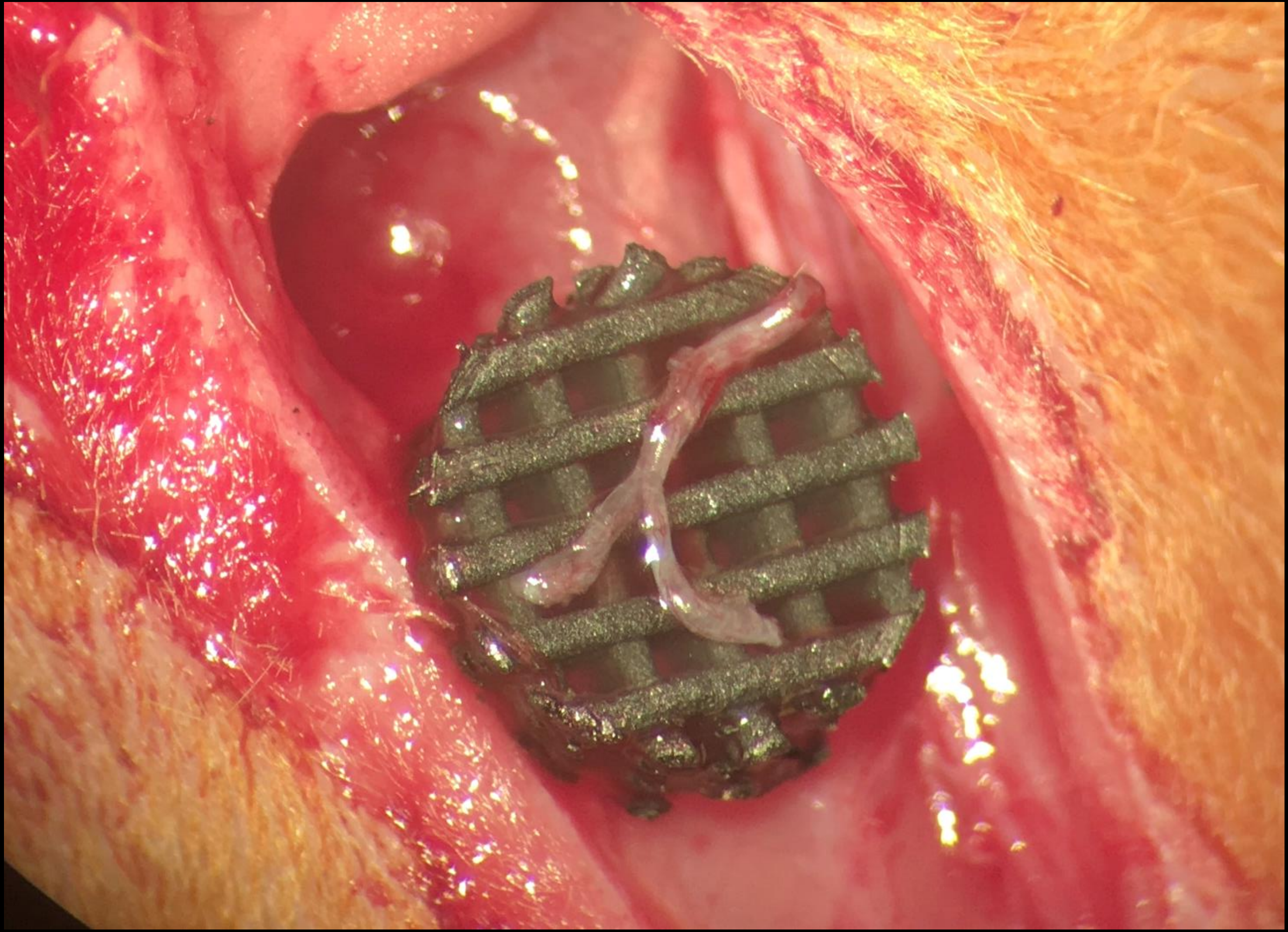




Wrap
Roll
Cut
Fold
Suture
Fuse
Adhere



Ongoing Innervation (Nerve into Muscle) Rat Model In Vivo Studies



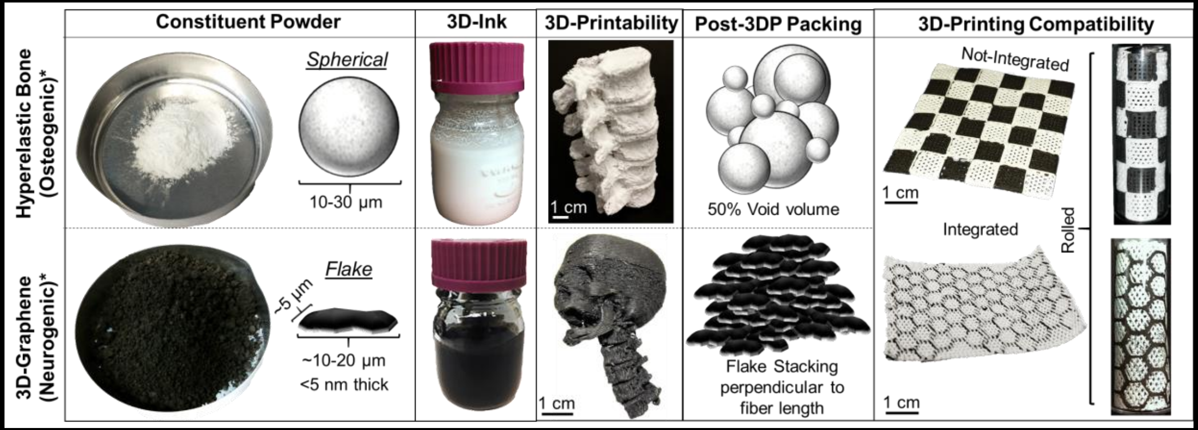
From few…

…To many

MULTI- & MIXED-MATERIAL 3D-PAINTING

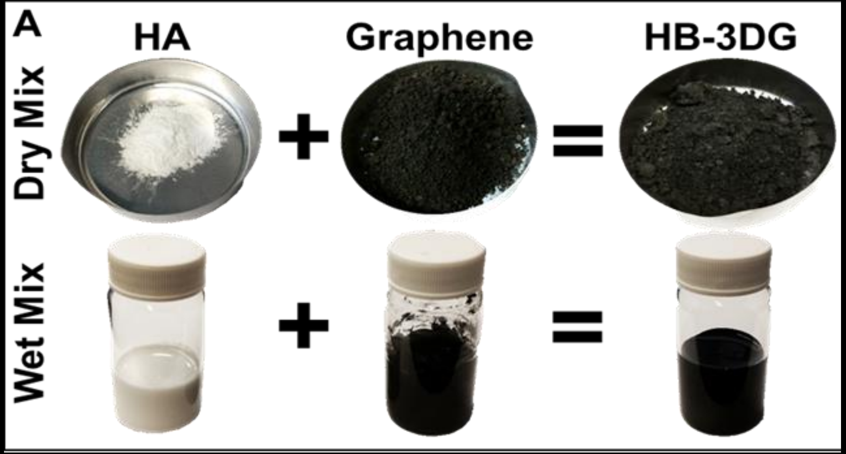
A. E. Jakus & R. N. Shah. **Multi and mixed 3D-printing of graphene-hydroxyapatite hybrid materials for complex tissue engineering.** *Biomedical Materials Research Part A;* 105A(1) A. 2017.

Towards an infinite 3D-ink palette… mixing 3D-inks



Separate inks can be co-3D-printed into multi-material systems

Compound inks can be made by mixing powders or already made inks



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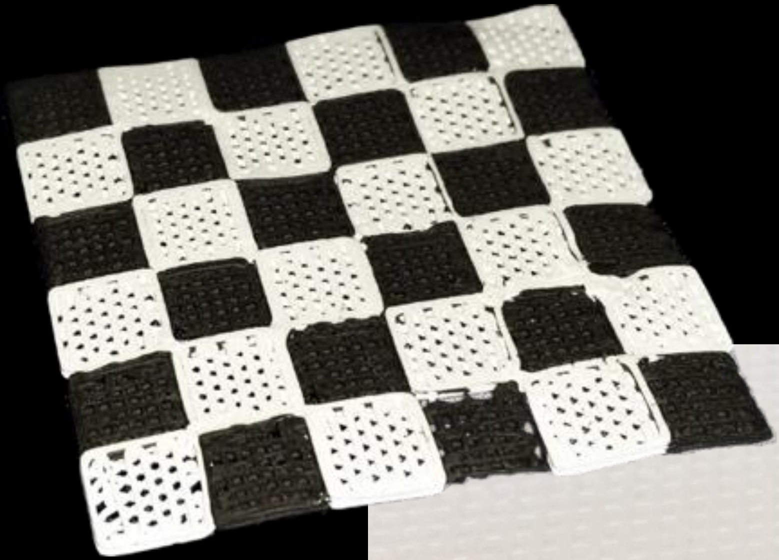


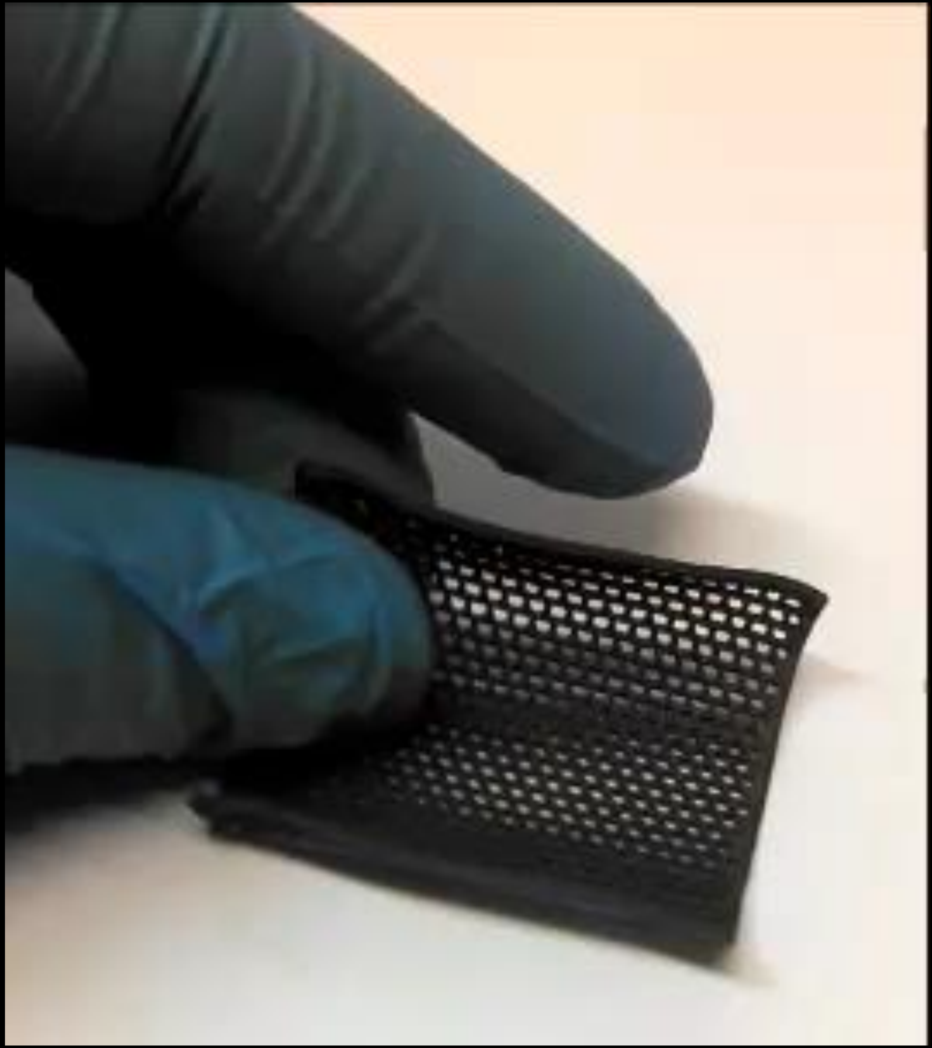
HB-3DG: 3D-Printability

Vertical

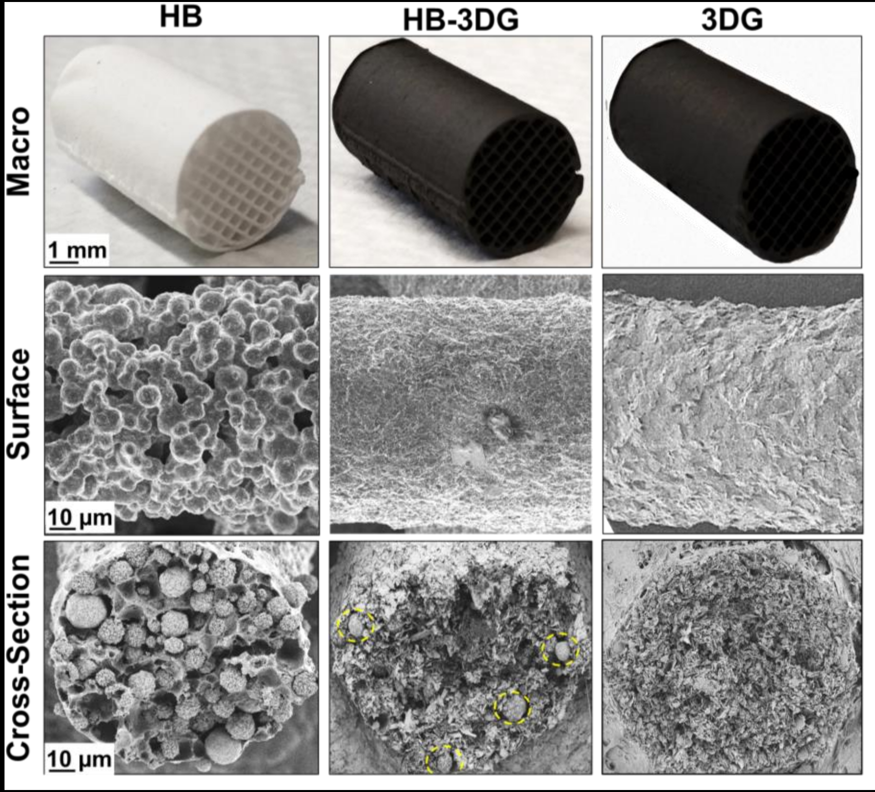
Large Area

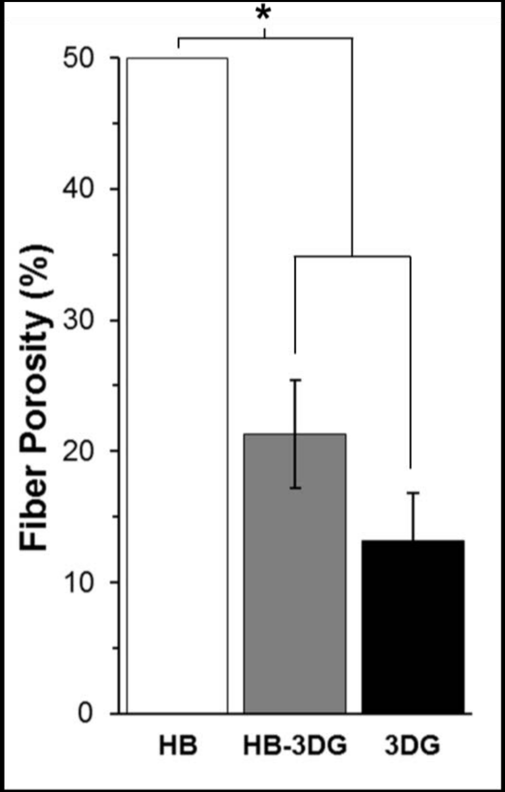
HB-3DG prints just as well as *Hyperelastic Bone* and *3D-Graphene*

Videos at 64x speed



Microstructure and Porosity

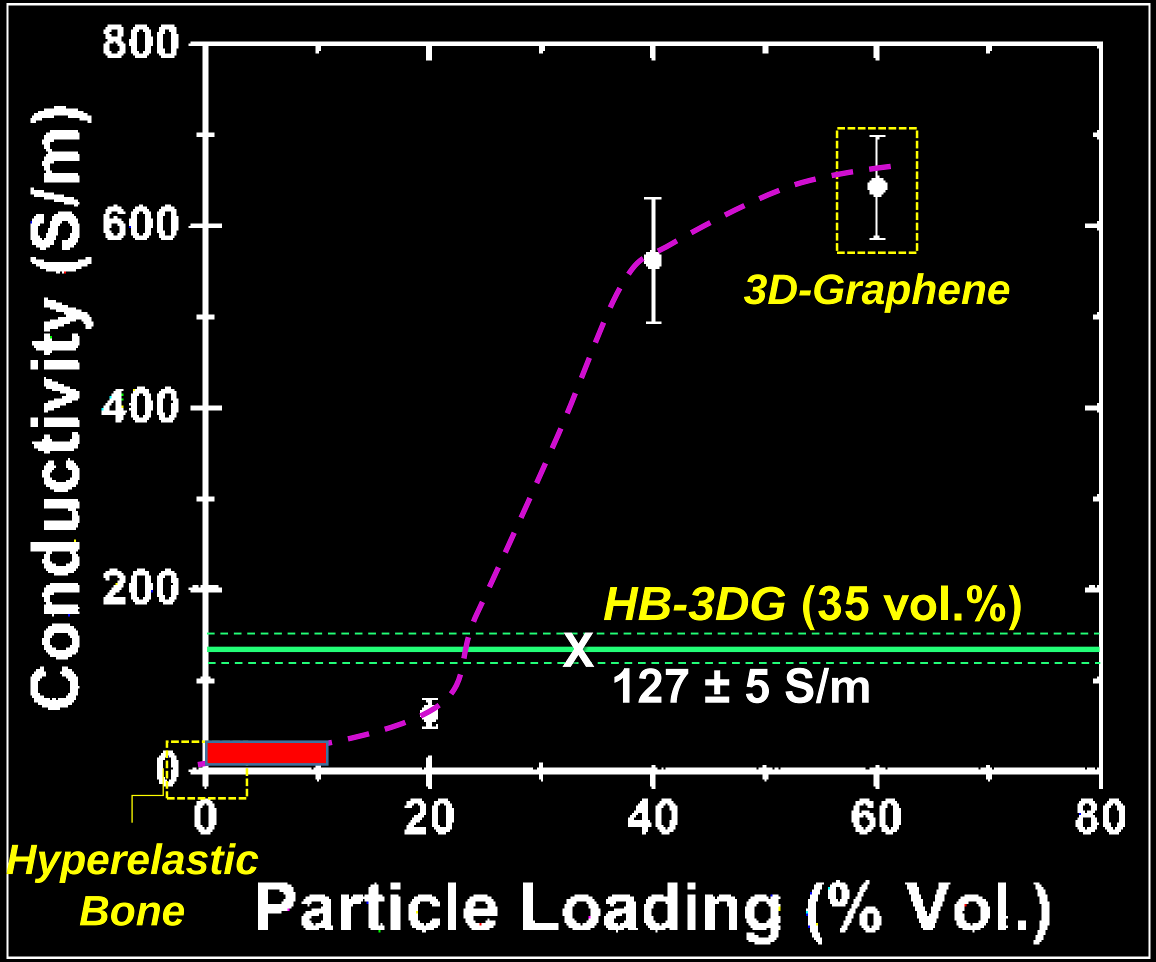




HB-3DG surface dominated by graphene
→ More similar to 3DG

HB-3DG Porosity
→ More similar to 3DG

Electrical Properties

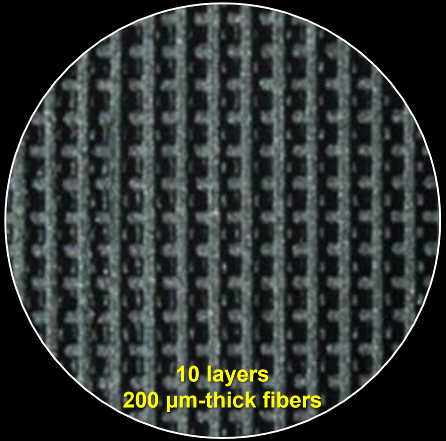


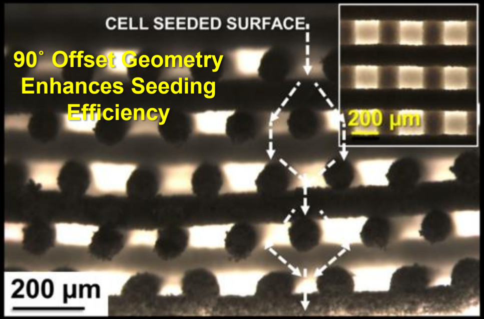
HB-3DG, although not as conductive as 3DG, still exhibits higher conductivity than the majority of previously reported systems

Typical particle loading and conductivities achieved by others in 3D printed carbon composite systems

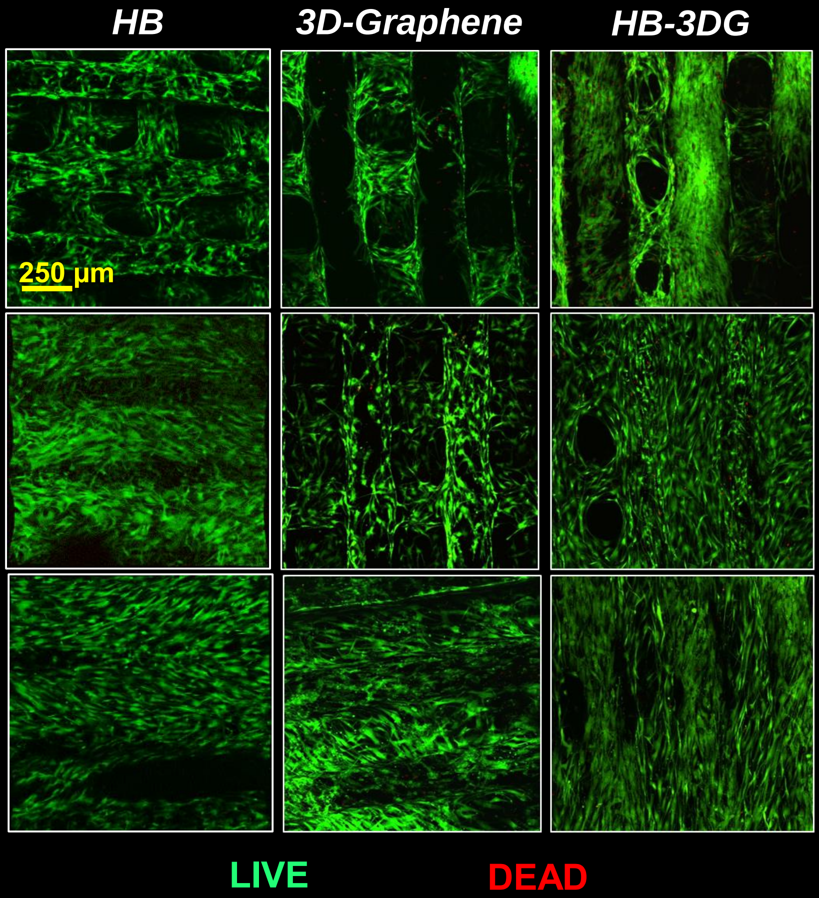
In Vitro Response

4 mm-diameter scaffolds punched from larger 3D-printed sheets

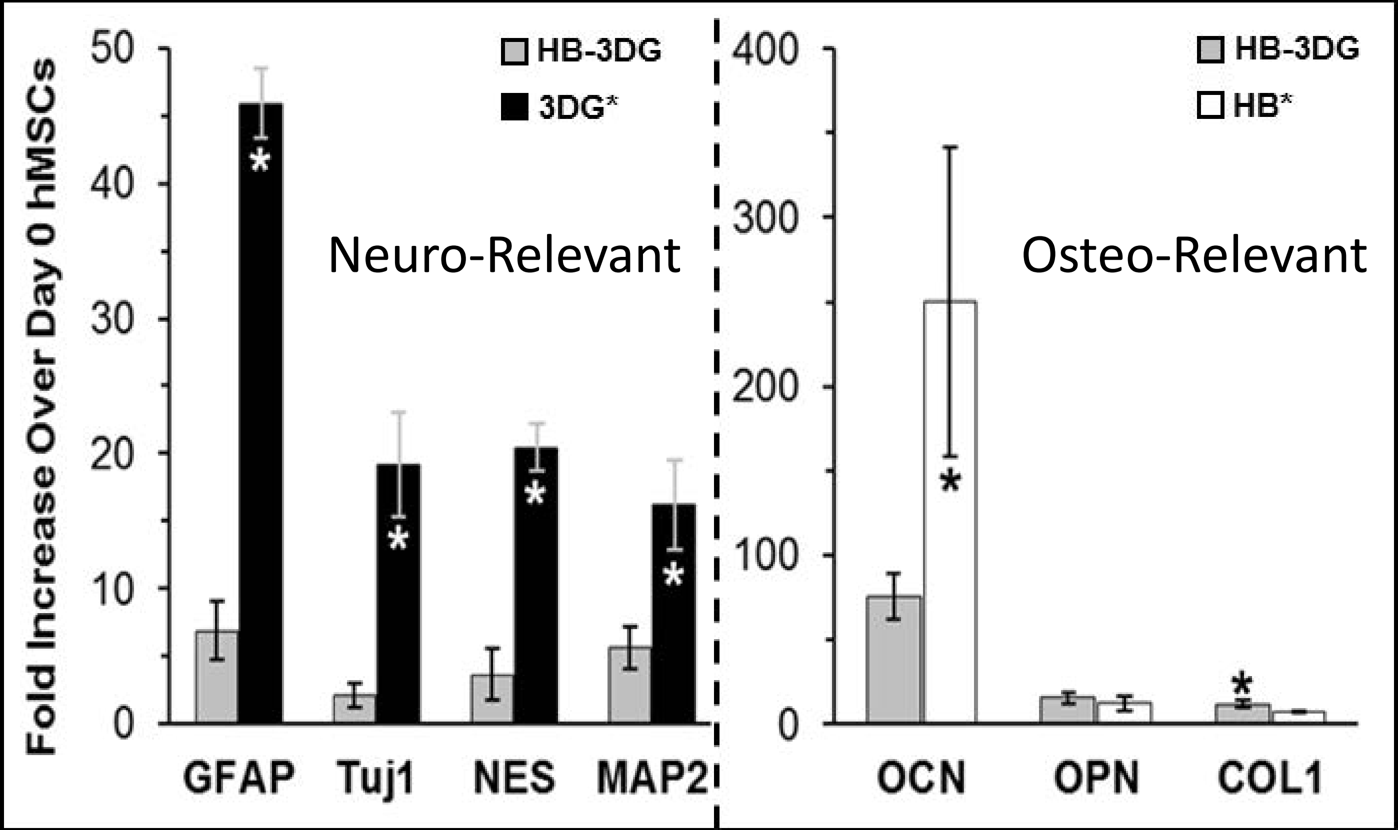




Seeded with 50k human mesenchymal stem cells



Tailoring Biological Properties with Mixed Inks

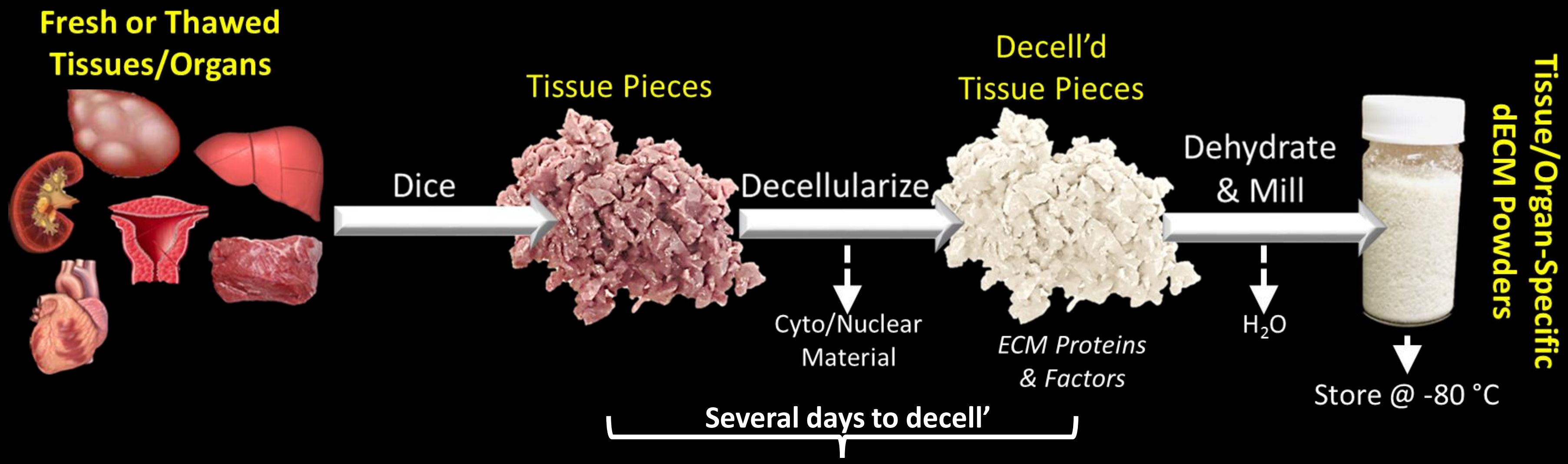


hMSCs HB-3DG show a mixed neuro/osteo response

“Tissue Papers” from Organ-Specific Decellularized Extracellular Matrices

Jakus AE, Laronda MM, Rashedi AS, Robinson CM, Lee C, Jordan SW, Orwig KE, Woodruff TK, Shah RN. Surgically friendly "Tissue Papers" from Organ-Specific Decellularized Extracellular Matrices. *Advanced Functional Materials* 2017. In Review.

What if the powder in 3D-Paint was biological tissue?

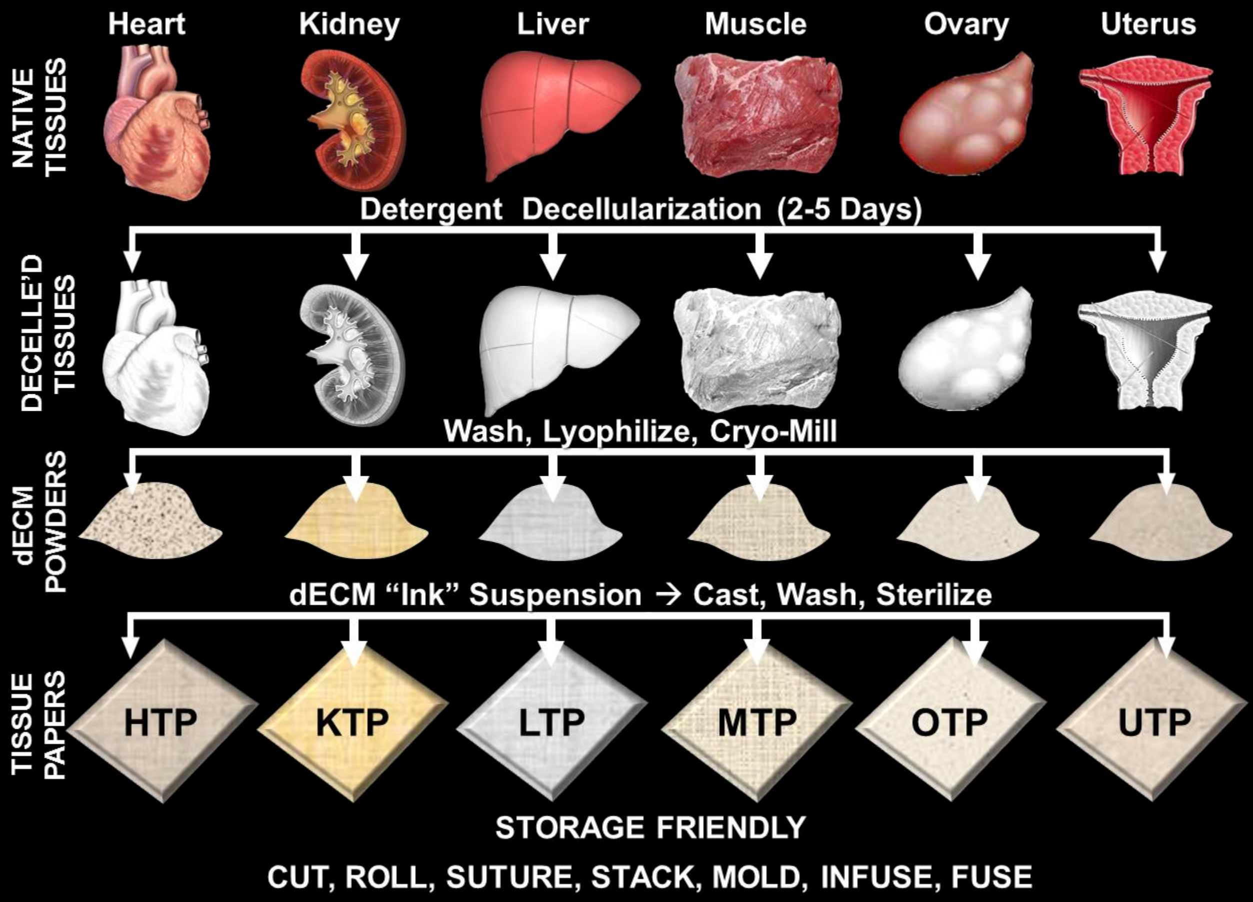


Day 0

Day 1

Day 2

"Tissue Paper" Fabrication – Process Conserved



60-70 vol.% dECM
30-40 vol.% PLGA

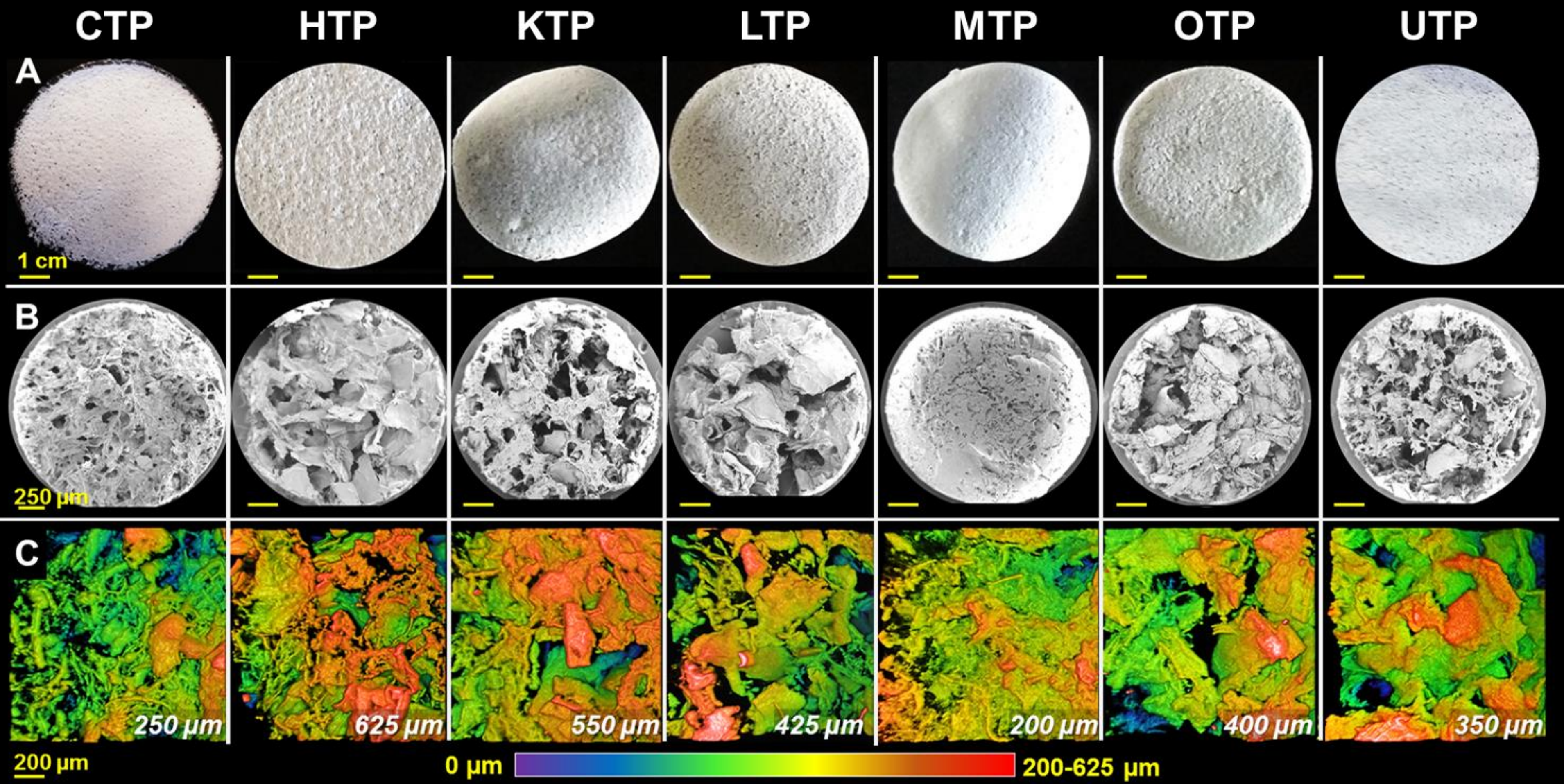
No elevated temperatures

No chemical digestion

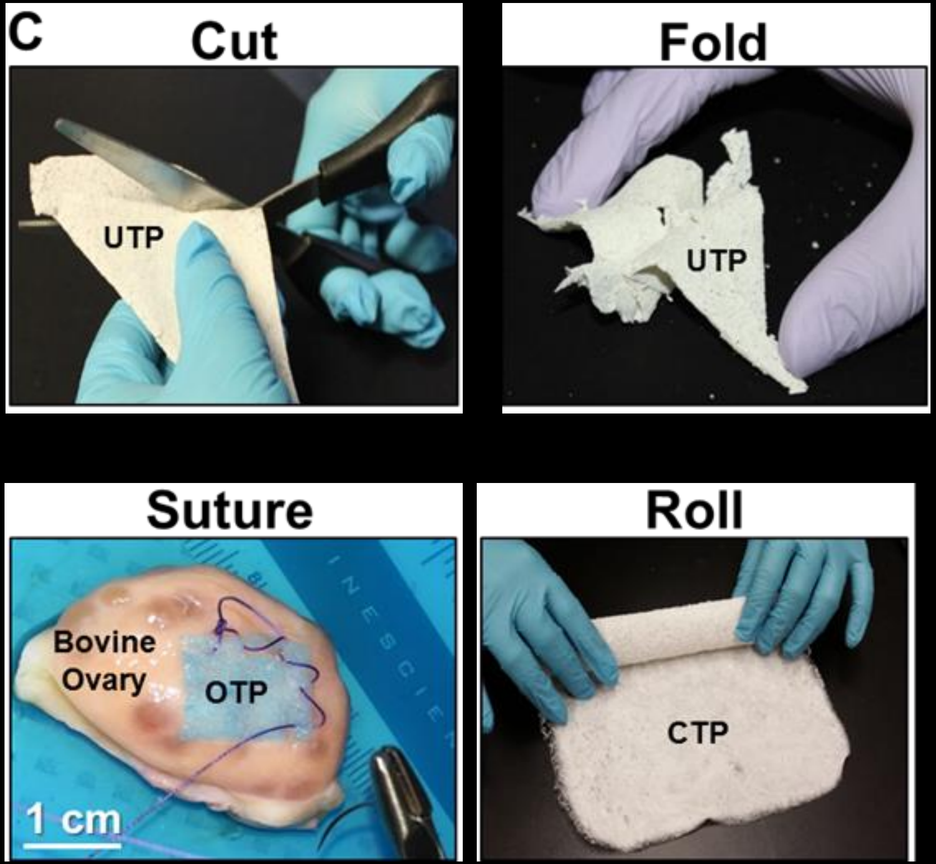
No chemical-crosslinking

Tissue Independent

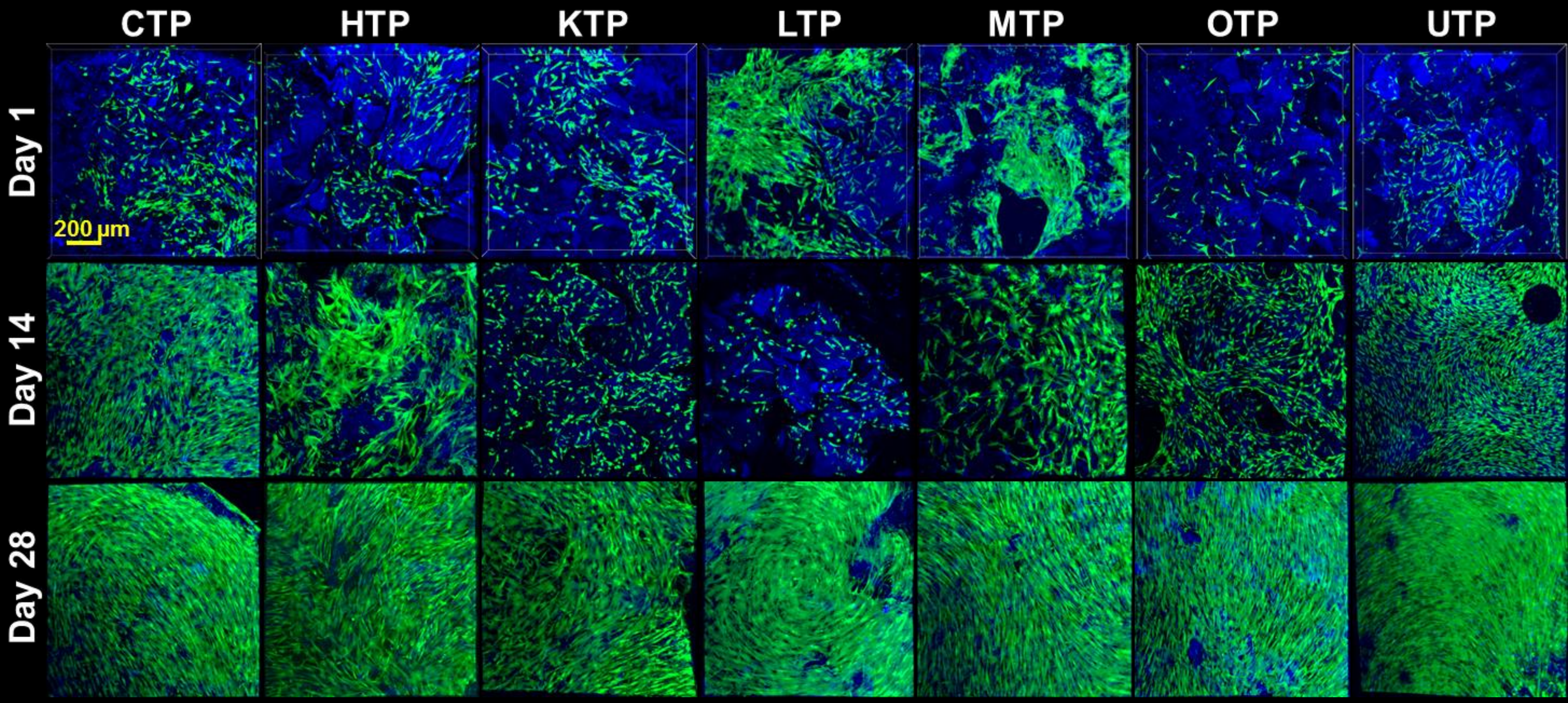
Tissue Papers - Microstructures and Collagen Content



Tissue Papers - Real World Handling

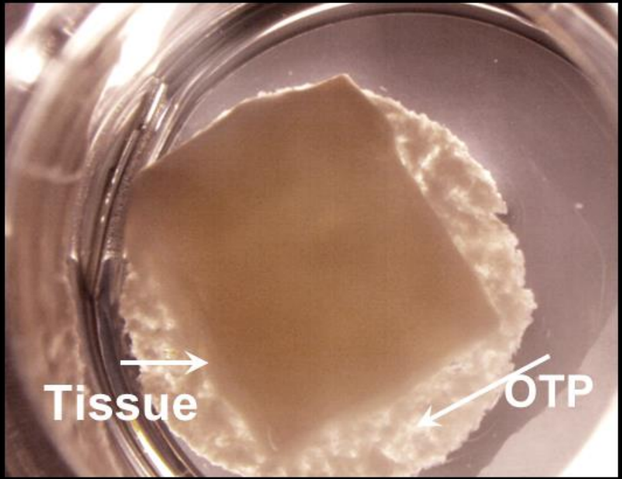


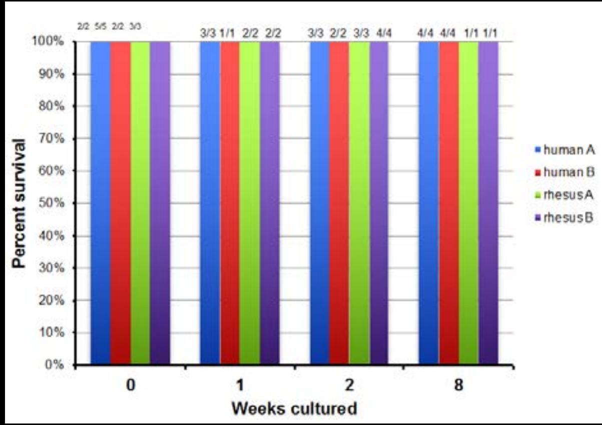
Tissue Papers - Human Mesenchymal Stem Cell Culture

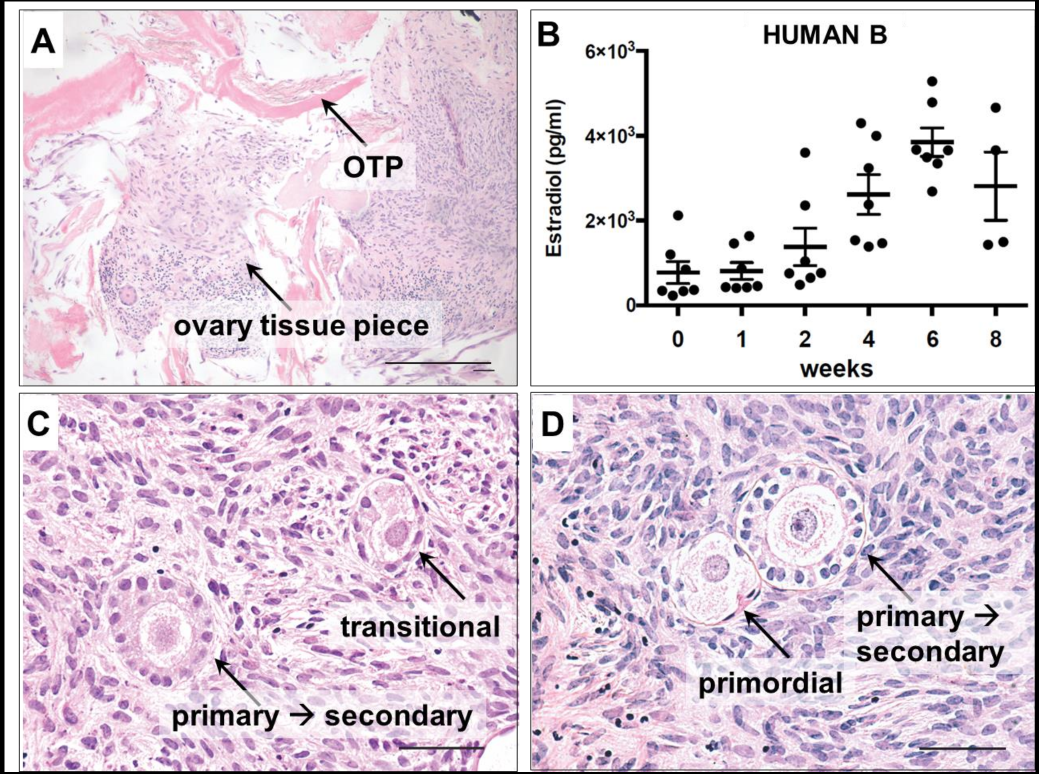


Green = Live Red = Dead Blue = TP (Collagen)

OTP - Rhesus and Human Ex Vivo Cortical Strip Culture







Preserved the health and function of human ovarian tissue more than 8 weeks after the donor had perished

In collaboration with Teresa Woodruff, PhD; Monica Laronda, PhD; Alexandra Rashedi

Tissue Paper - Additional Versatility

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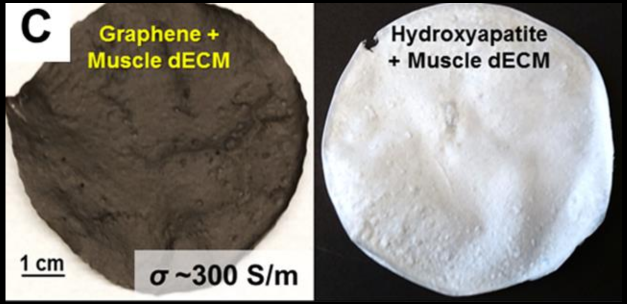
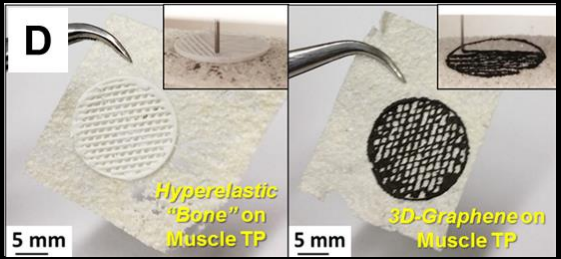
Scale

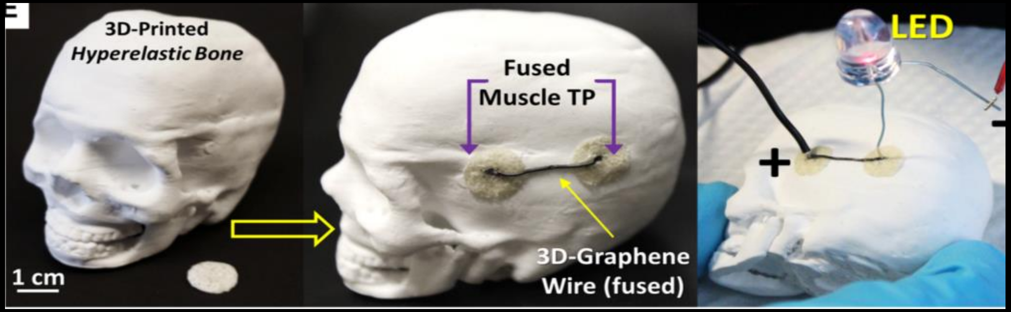


Hybrids

Cast into molds

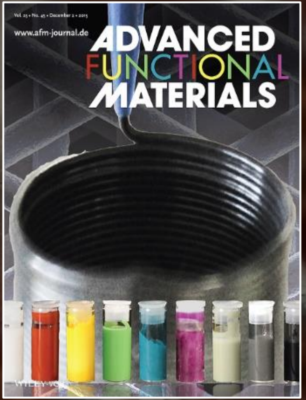


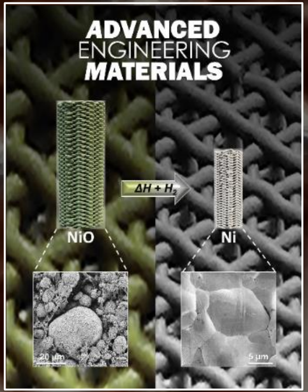
3D-Printing Substrates



"Graft" onto 3DP structures

Metallic Architectures from 3D-Printed Powder-Based Liquid Inks





Jakus AE, Taylor SL, Geisendorfer NR, Dunand DC, Shah RN. Metallic Architectures from 3D-Printed Powder-Based Liquid Inks. Advanced Functional Materials 2015;25(45):6985-6995.

Taylor SL & Jakus AE, Shah RN, Dunand DC. Iron and Nickel Cellular Structures by Sintering of 3D-Printed Oxide or Metallic Particle Inks. Advanced Engineering Materials 2016; In Press.

"TRADITIONAL" METAL AM

ENERGY-BASED
"Additive Manufacturing"

Laser Sintering
(Powder Bed)

Laser Melting
(Powder Bed)

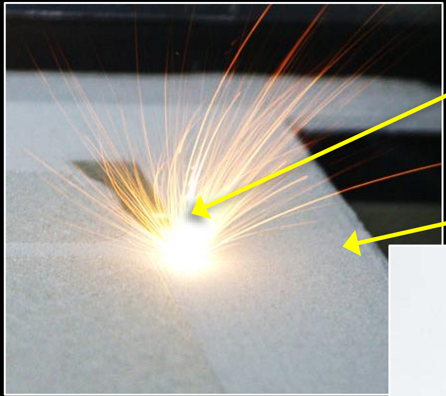
Laser Metal Deposition

Electron Beam Melting
(Powder Bed)

Originally Pioneered by *3D Systems*

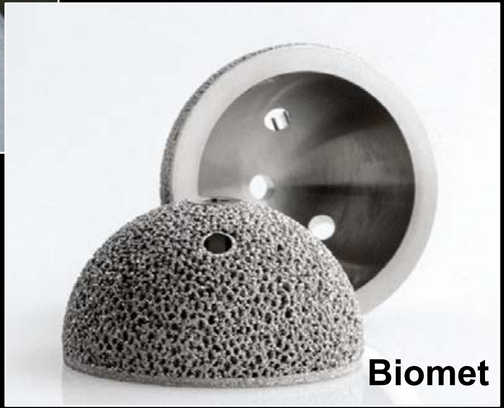
Stereolithography *(not for metals)*
(Monomer Bath)

Instrument Driven



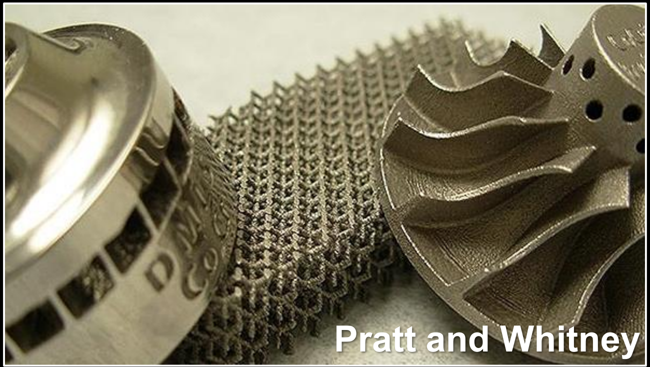
High-power energy beam

Powder-Bed

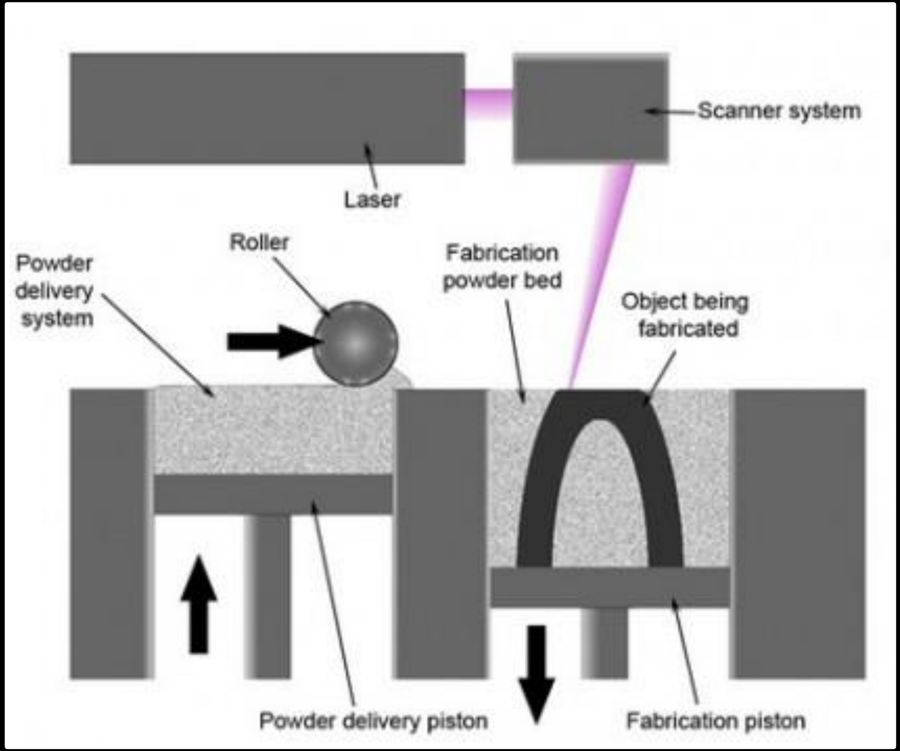


An established process:

Been in use for 30 years



"TRADITIONAL" METAL AM → POWDER-BEDS + ENERGY



Generic Powder-Bed + Energy Scheme

Material Criterion

1) Chemically stable powders (pre-alloyed)
2) Specific powder size and morphology
3) Can be sintered or melted rapidly (excludes most ceramics and many metals and alloys)
4) Does not reflect or scatter energy beam

Parts must be extracted from powder bed and cleaned after completion

Metals and Alloys from 3D-Painted Rusts

$- O_2$

From Raw Oxide Powder to Metallic Architecture

Mix with solvents and elastomer

3D-print via extrusion

$H_2 + \Delta H$

Oxide Powder(s) (1-10 μm, spherical)

3D-Ink

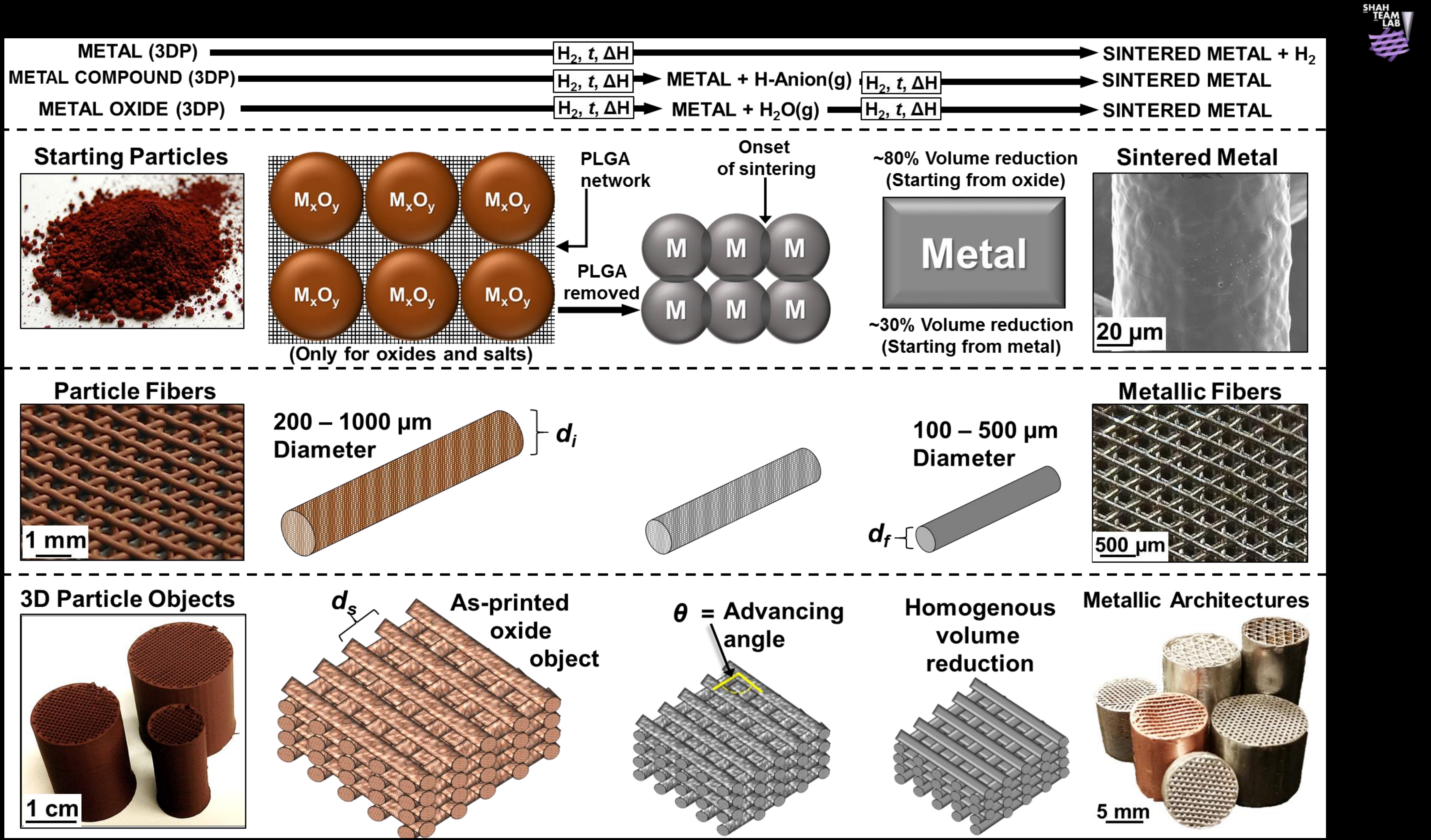
Oxide Green-Body

Metallic Counterpart

Scalable synthesis

Rapid
No dry time

Homogeneous reduction



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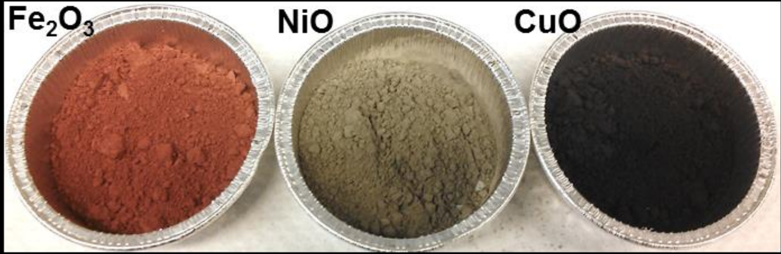
METAL (3DP)
H2, t, ΔH
SINTERED METAL + H2
METAL COMPOUND (3DP)
H2, t, ΔH
METAL + H-Anion(g)
H2, t, ΔH
SINTERED METAL
METAL OXIDE (3DP)
H2, t, ΔH
METAL + H2O(g)
H2, t, ΔH
SINTERED METAL
Starting Particles
MxOy
PLGA network
PLGA removed
(Only for oxides and salts)
Onset of sintering
M
~80% Volume reduction (Starting from oxide)
Metal
~30% Volume reduction (Starting from metal)
Sintered Metal
20 µm
Particle Fibers
1 mm
200 – 1000 µm Diameter
di
100 – 500 µm Diameter
df
Metallic Fibers
500 µm
3D Particle Objects
1 cm
ds
As-printed oxide object
θ = Advancing angle
Homogenous volume reduction
Metallic Architectures
5 mm

Oxide Powders and 3D-Inks

Single Oxide Inks

Typically, 1-10 µm or -325 mesh (commercial)



Fe_2O_3 NiO

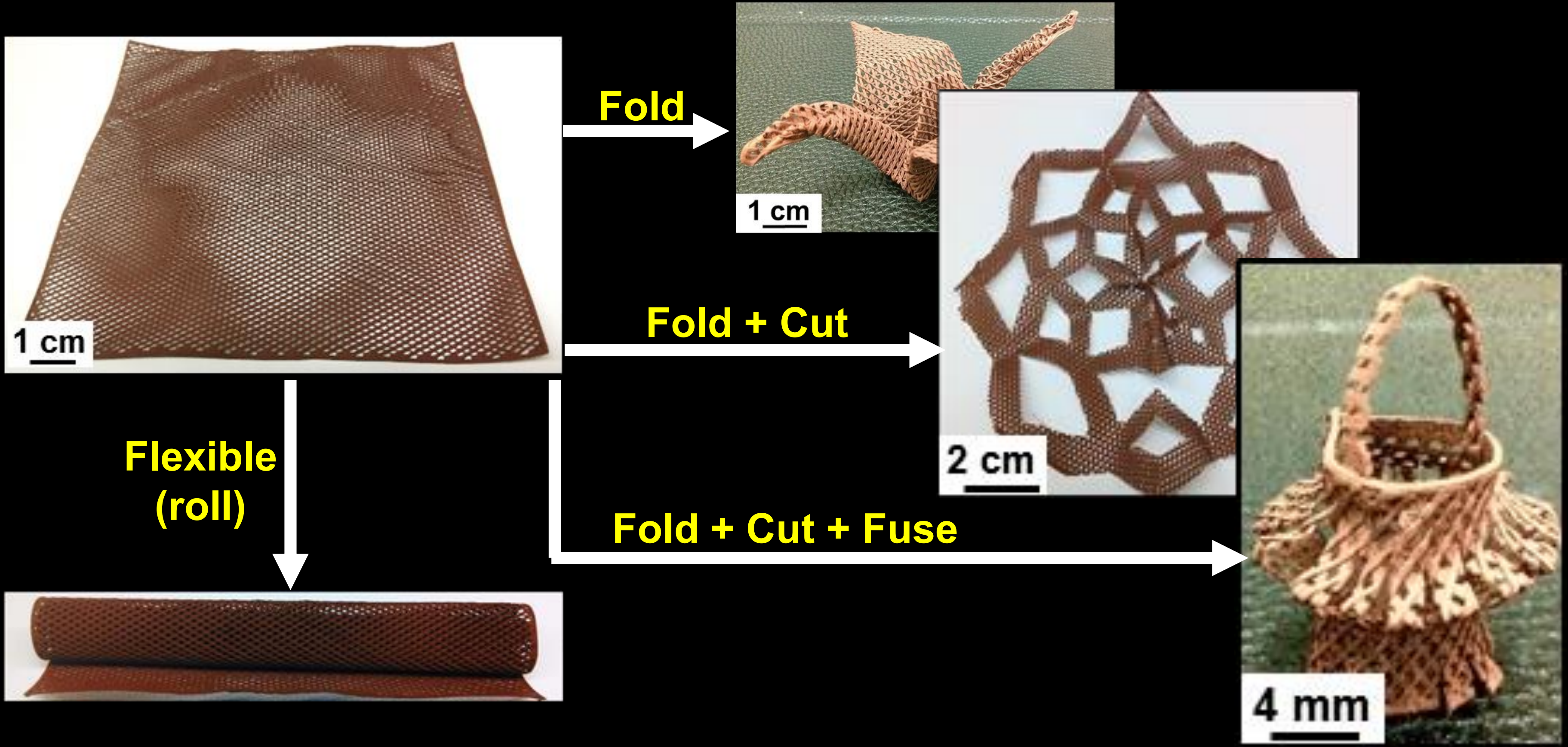
Dry powder mix → Make Ink

Wet mix pre-made inks

Multi-Oxide Inks

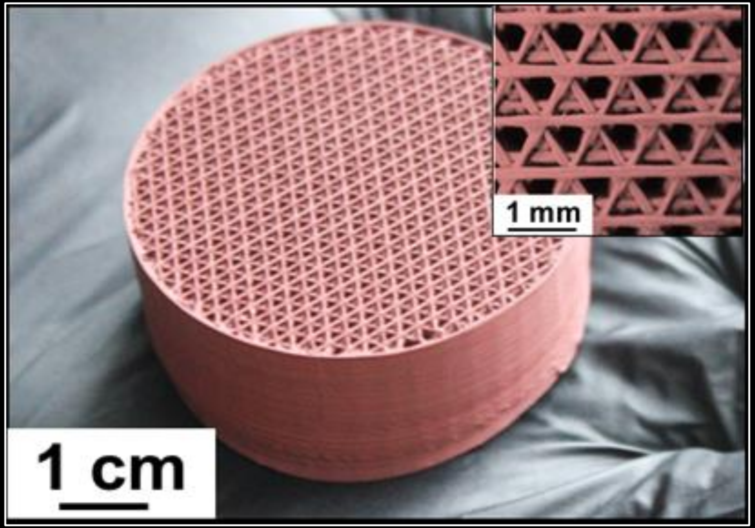
Ink synthesis independent of powder chemistry

Manipulating Iron Oxide Sheets



No need to re-wet. Remain flexible for at least 4 years.

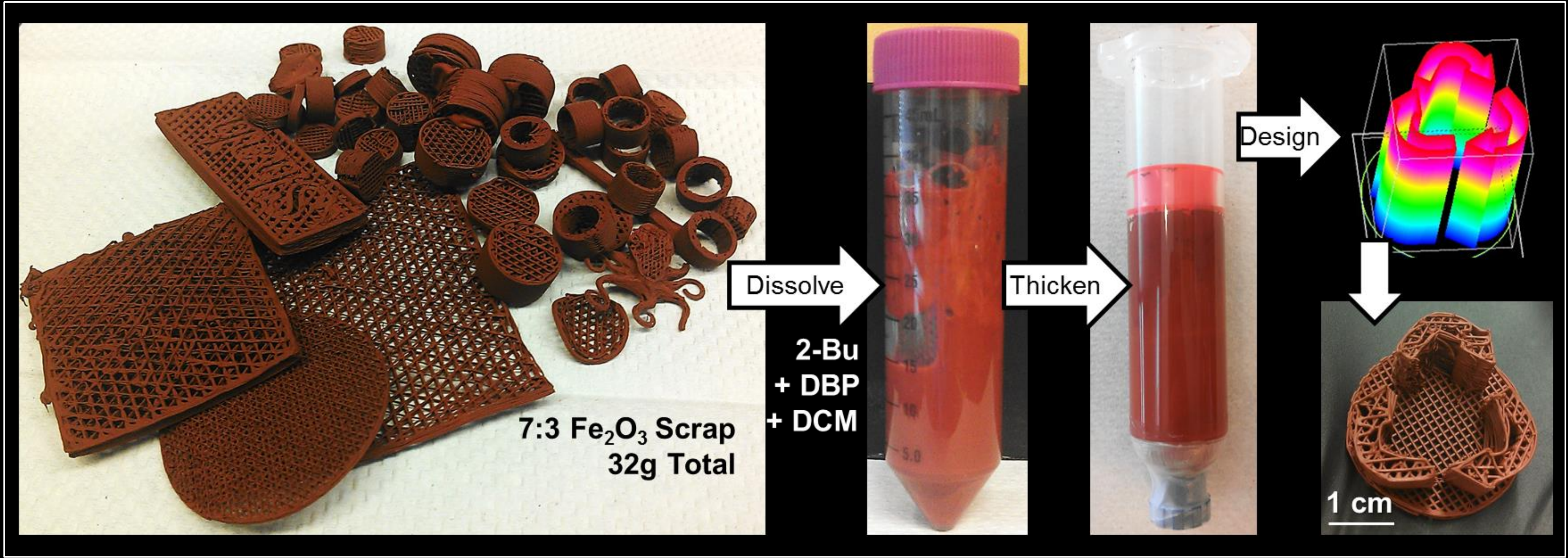
3D-Printing → Thick & High Aspect Ratio



Speed → < 15 minutes to 3D-print

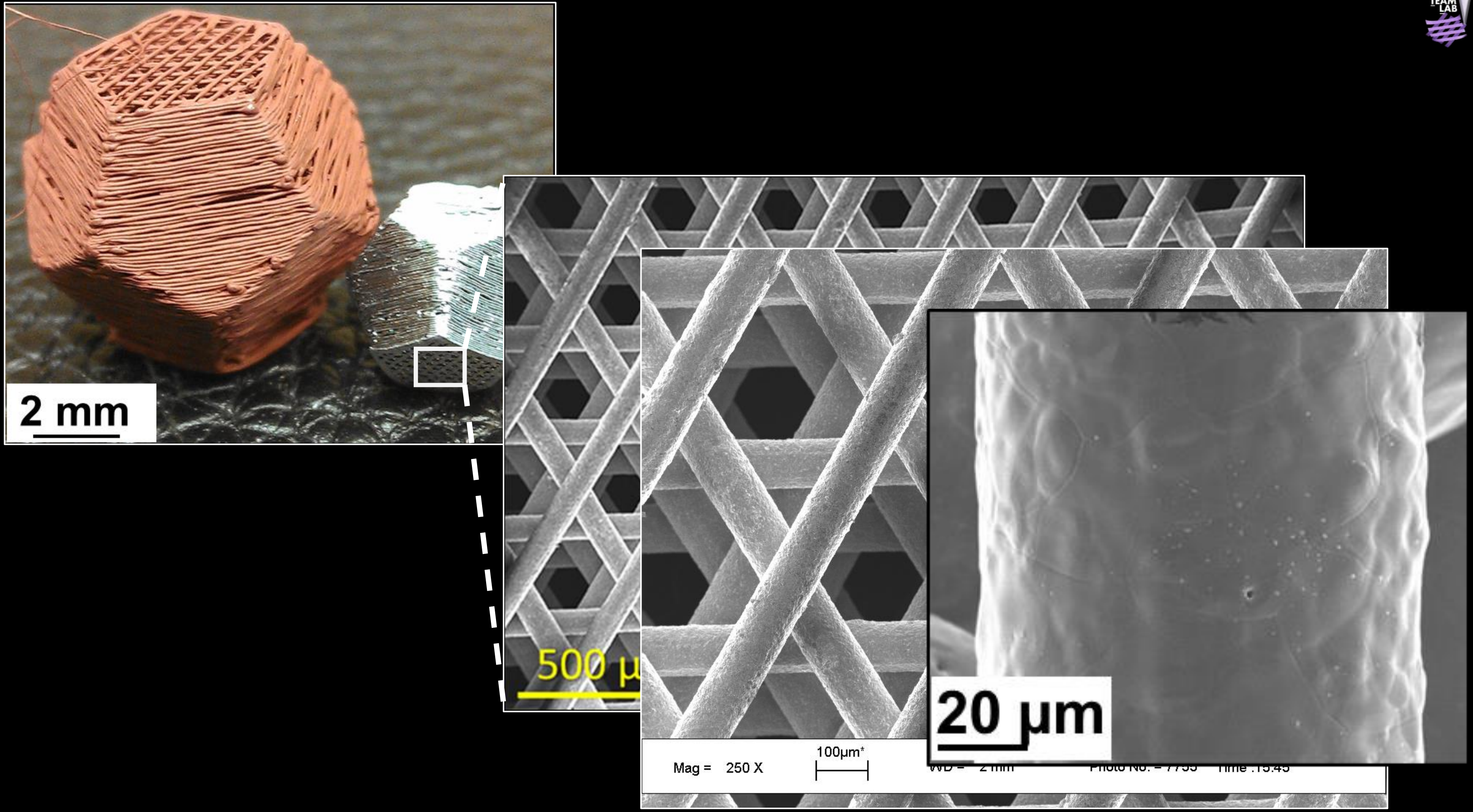
Many hundreds of 3D-printed layers (Currently limited by build space of 3D-printer)

Recycling Scrap Material

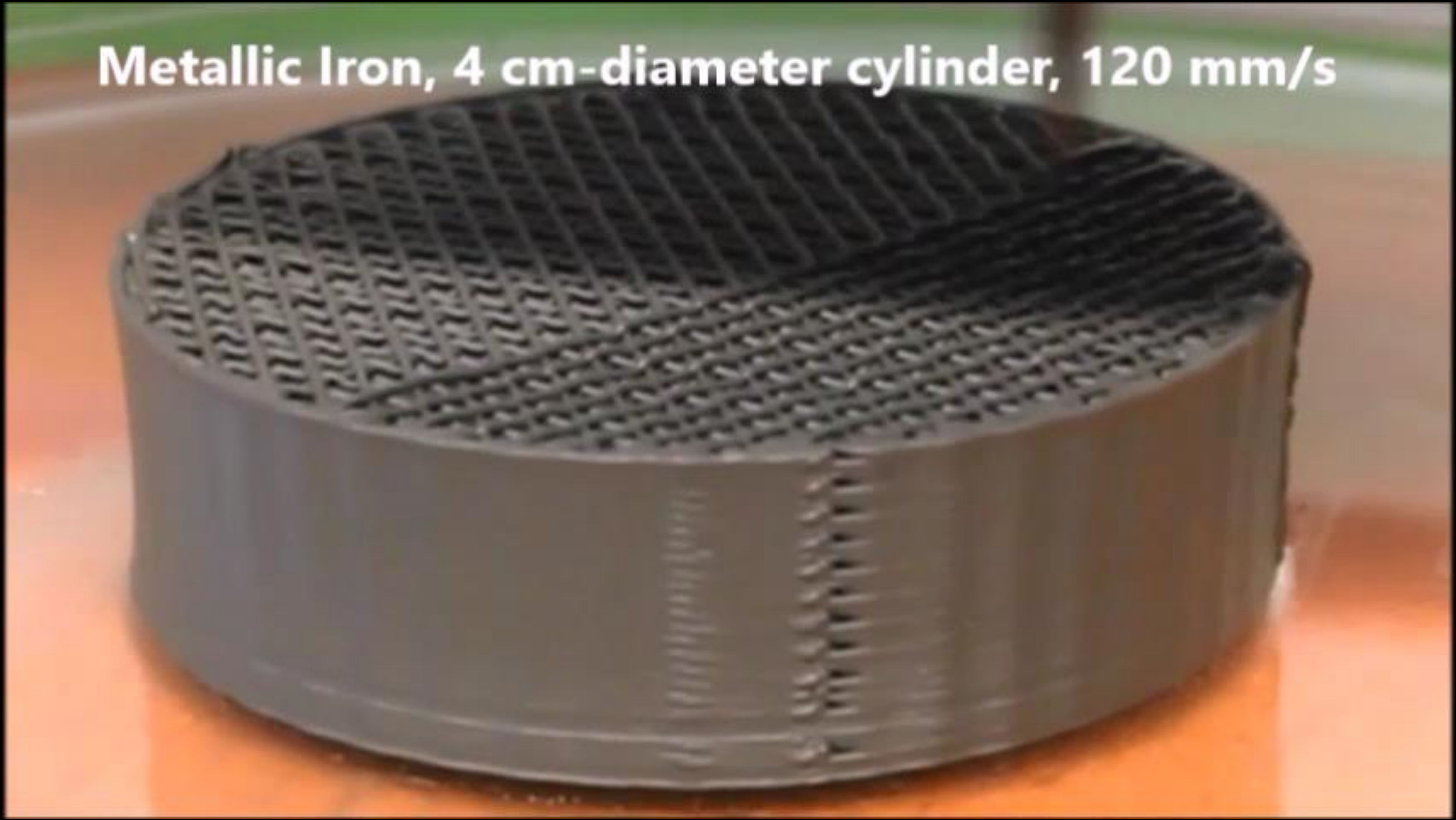


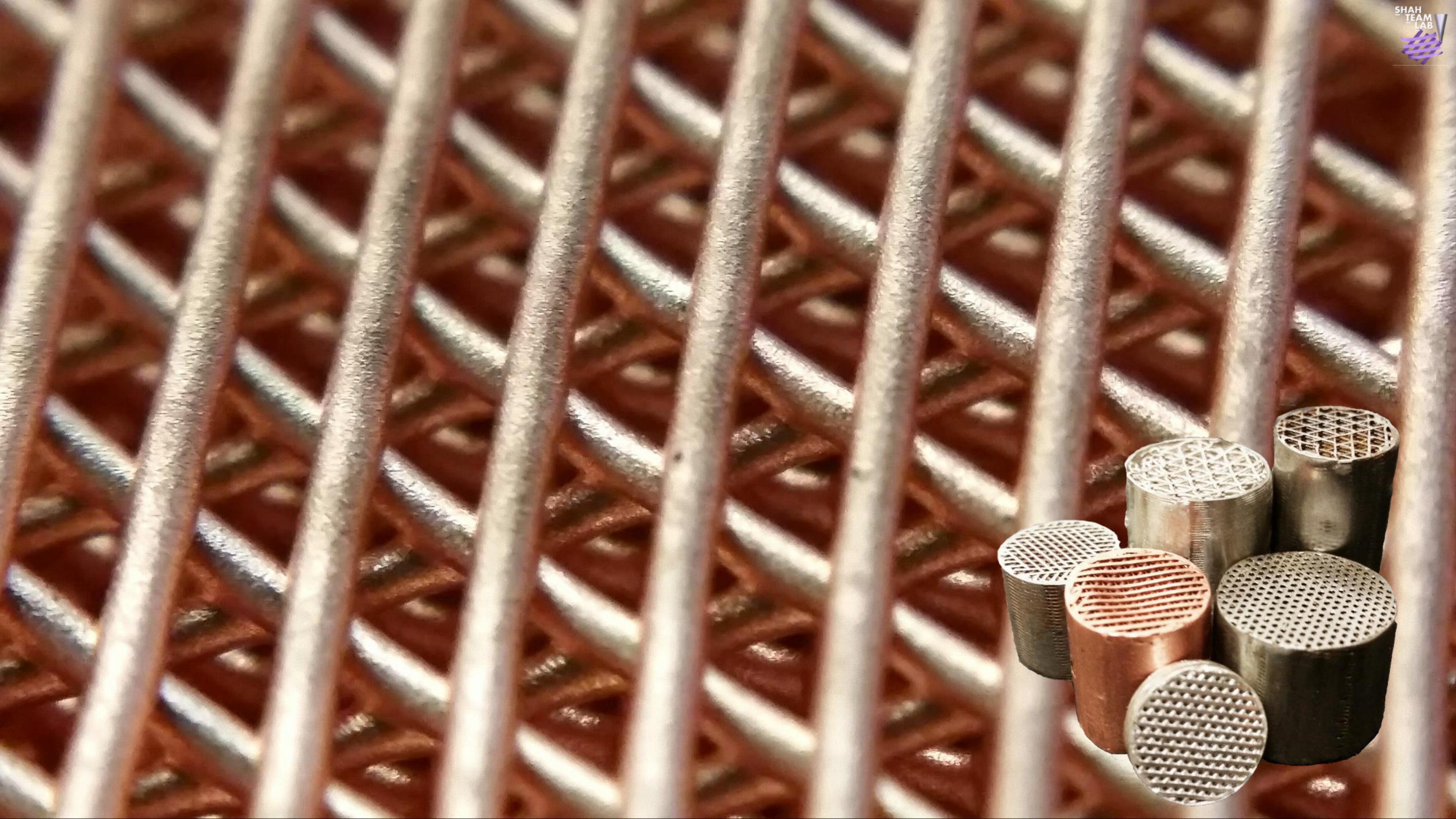
Scrap material can be dissolved/suspend in appropriate quantity of solvents to make 3D-printable ink


1 cm
5 mm
5 mm
3 mm
1 cm
2 mm
Fused Halves
1 mm
Cut
5 mm
5 mm
Cut
Cut
1 cm
5 mm
Shah
Shah
5 mm

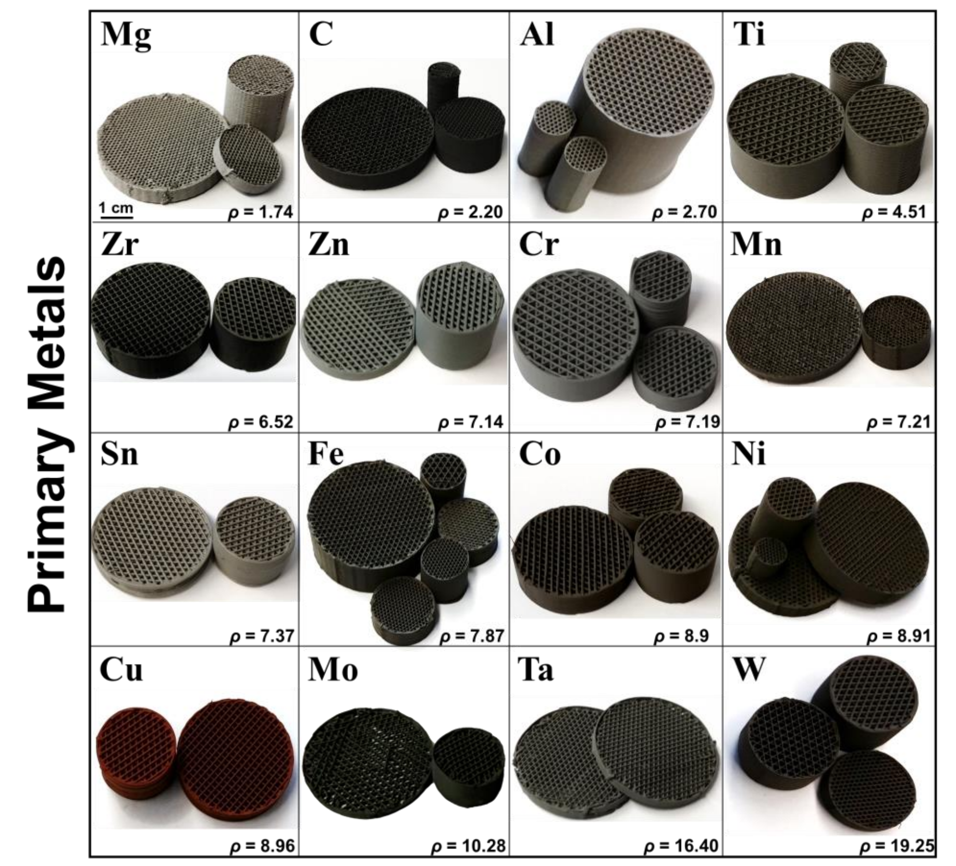

2 mm
500 µ
Mag = 250 X
100µm*
20 µm

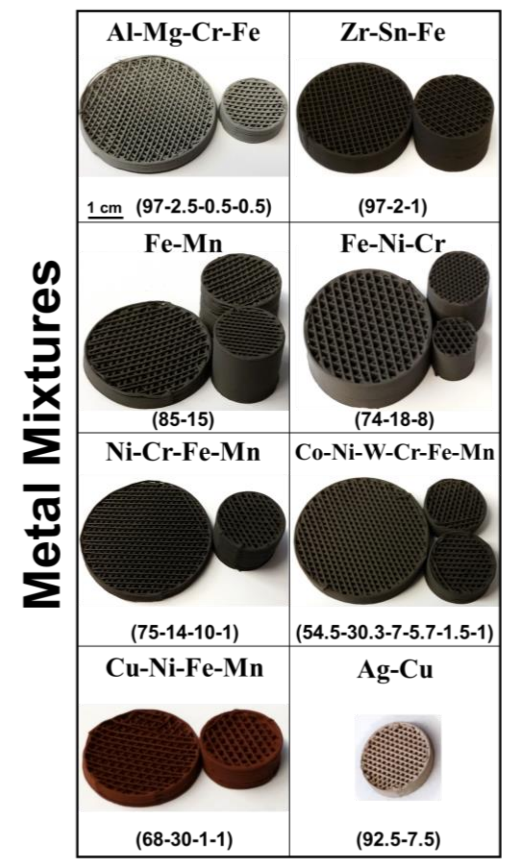
3D-Printing Metals and Other Compounds

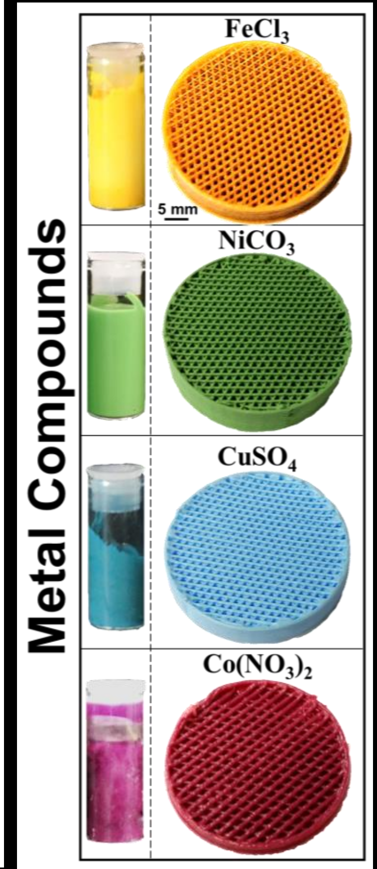



SHAH
TEAM
LAB

Further Expanding the 3D-Paint Palette…







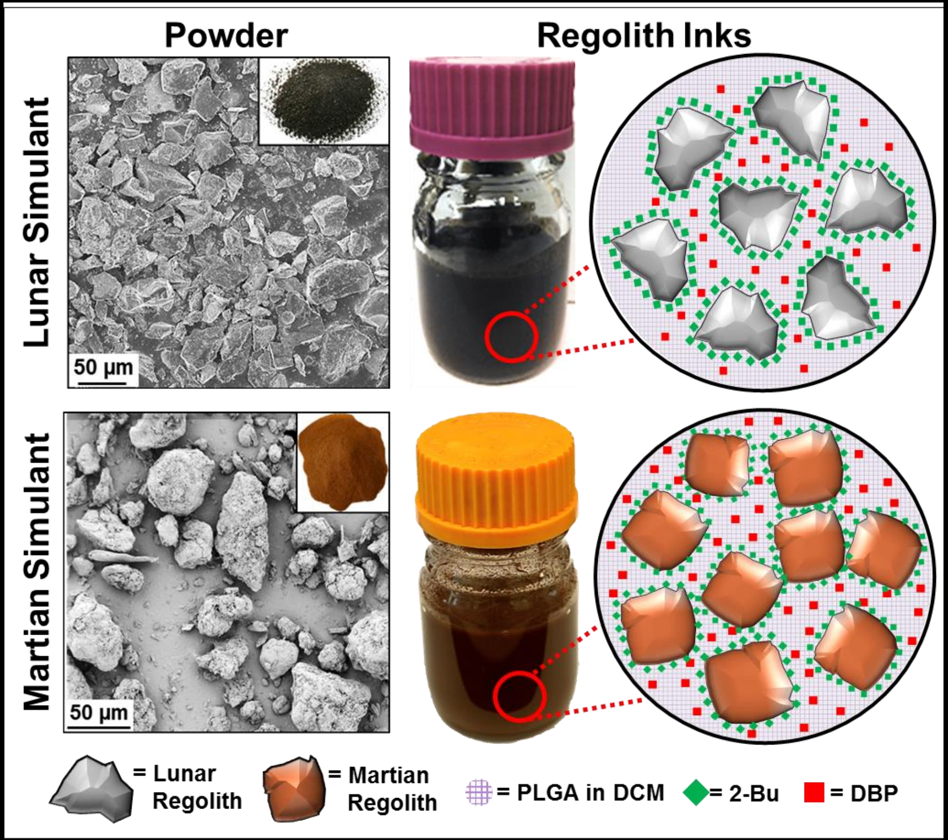
3D-Paint synthesis and 3D-printing behavior independent of powder

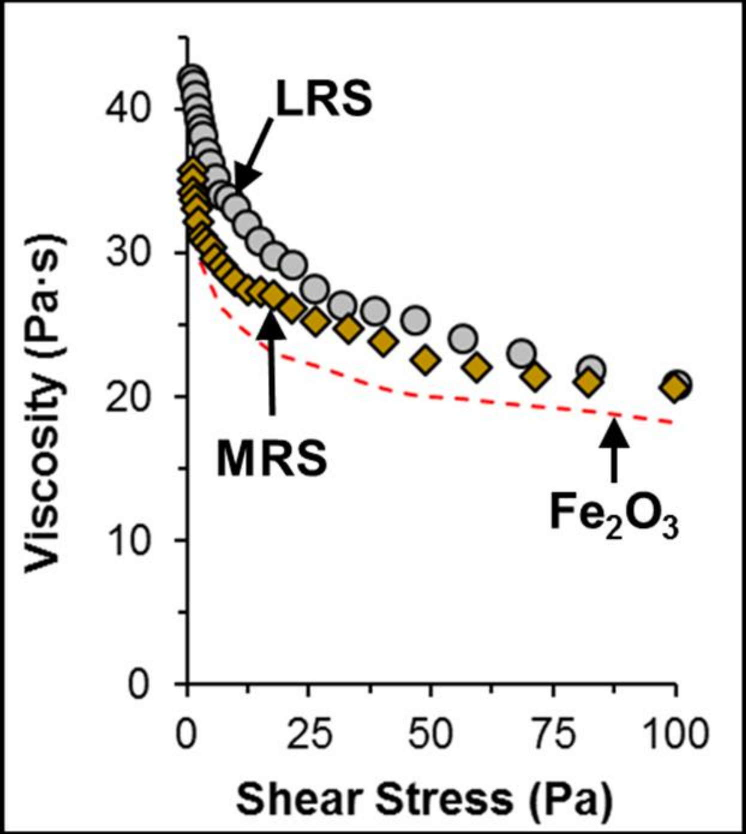
ROBUST AND ELASTIC LUNAR AND MARTIAN STRUCTURES FROM 3D-PRINTED REGOLITH INKS

Jakus AE, Koube KD, Geisendorfer NR, Shah RN. Robust and Elastic Lunar and Martian Structures from 3D-Printed Regolith Ink. Scientific Reports. 2017; 7(44931).

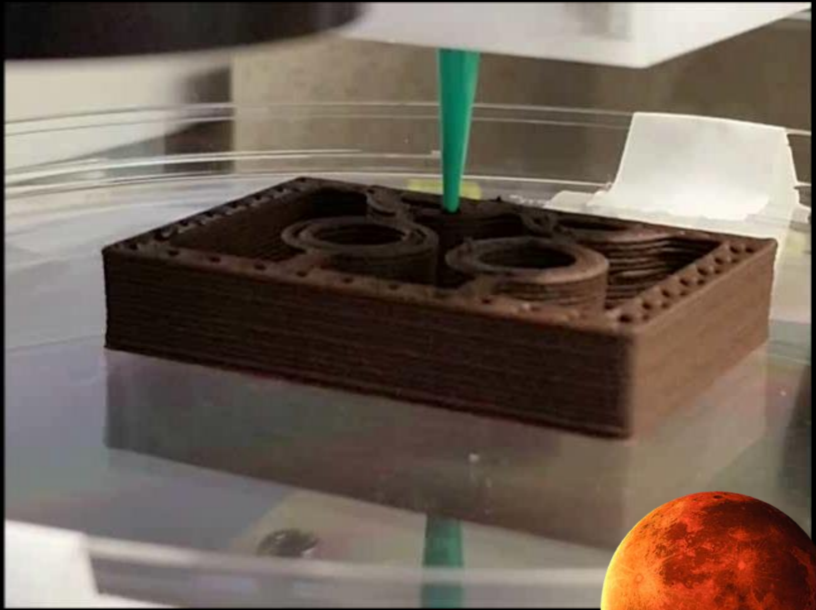
NASA.Gov

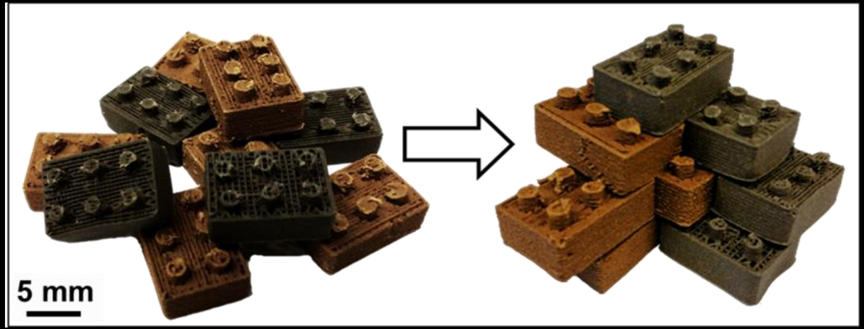
Lunar (LRS) and Martian (MRS) Inks





Despite distinct particle morphologies, LRS and MRS inks behave very similarly

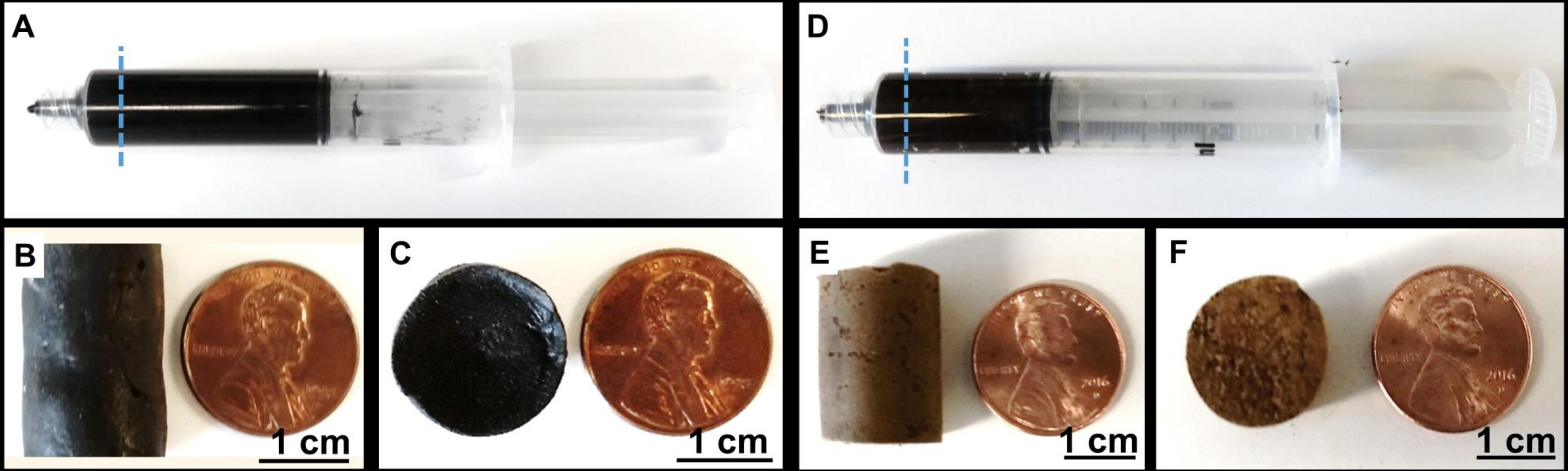



5 mm

LRS and MRS Large Diameter Extrusion Demonstration

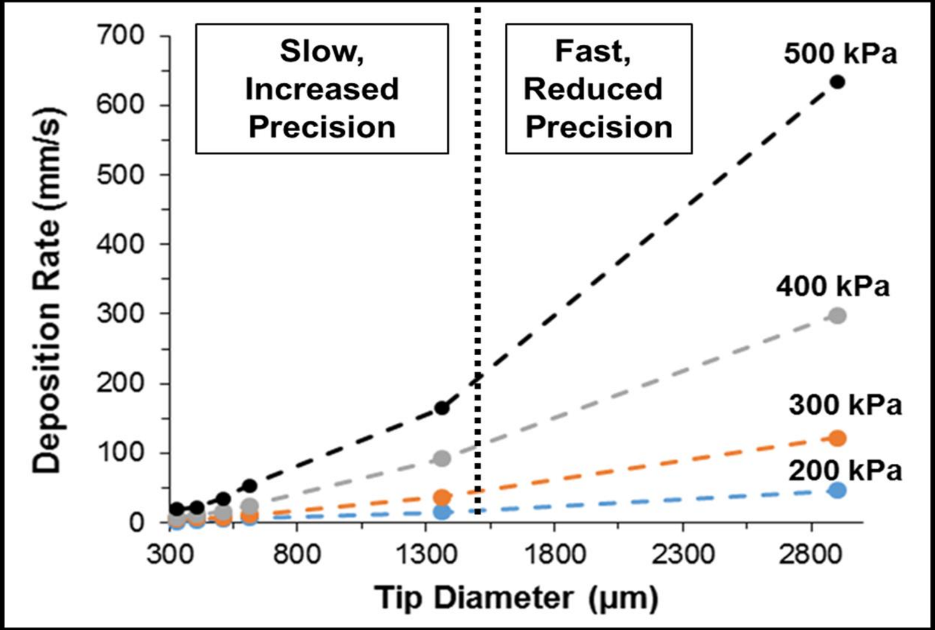
Lunar Regolith Simulant

Martian Regolith Simulant

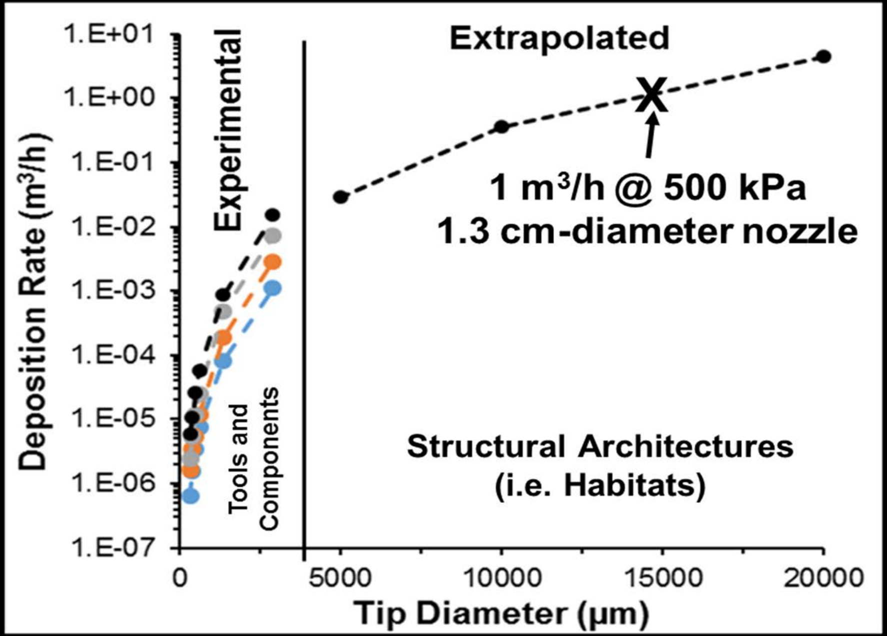


LRS and MRS Deposition Rates

Linear Deposition Rates

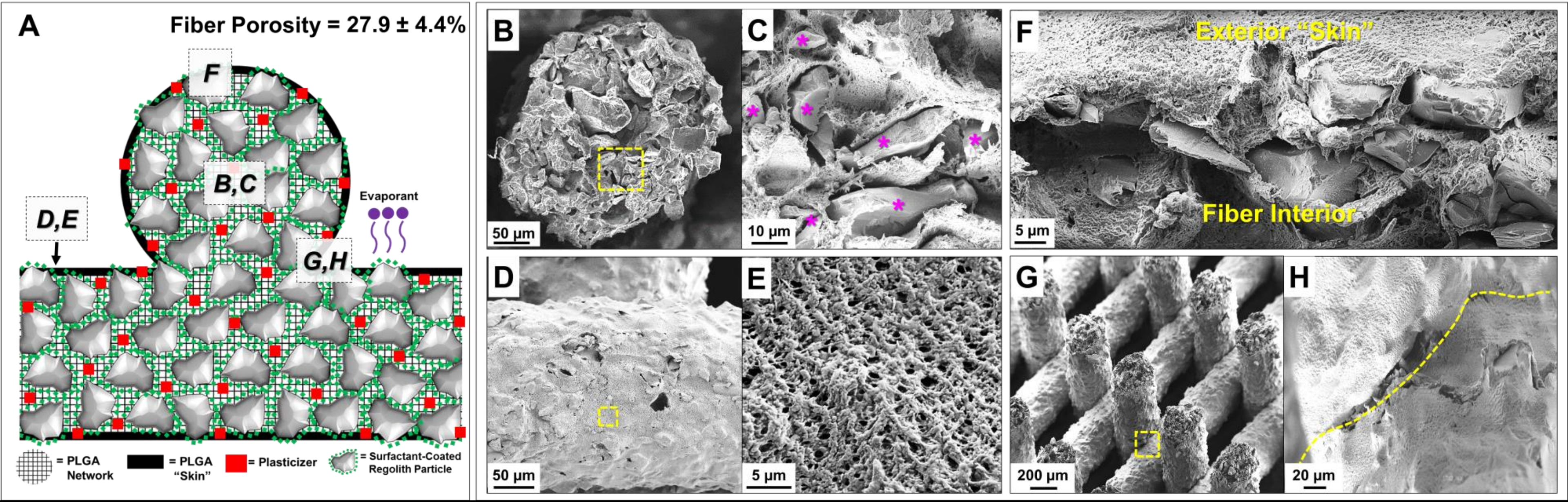


Volumetric Deposition Rates

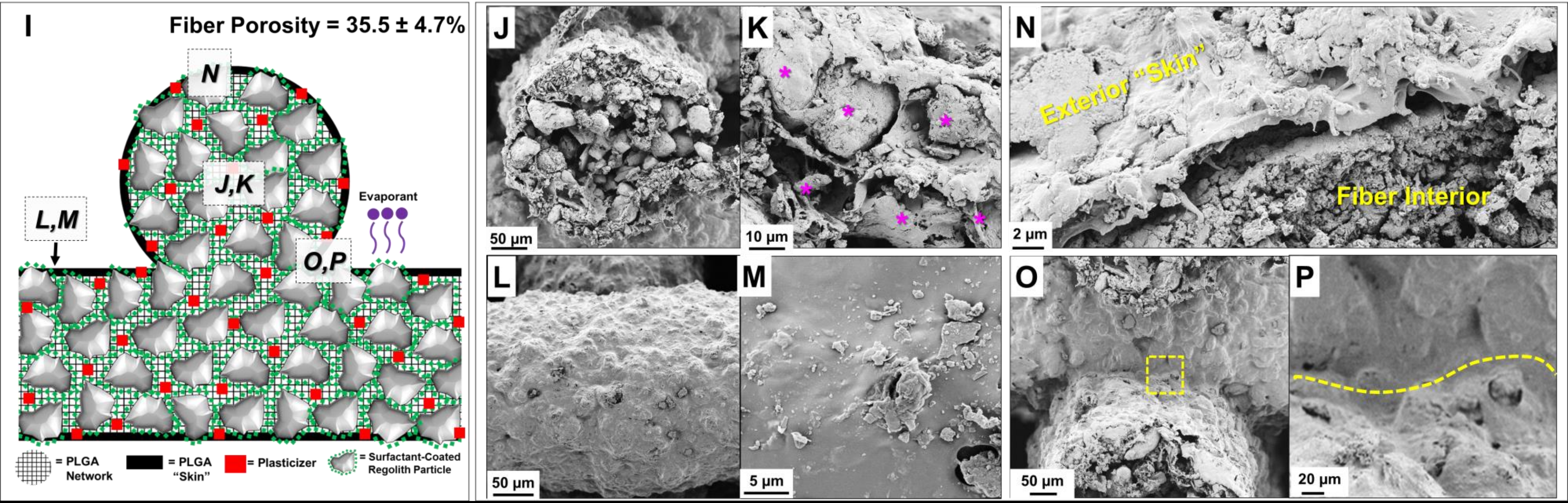


3D-Printable over a wide range of parameters (speed, pressures, nozzle diameter)

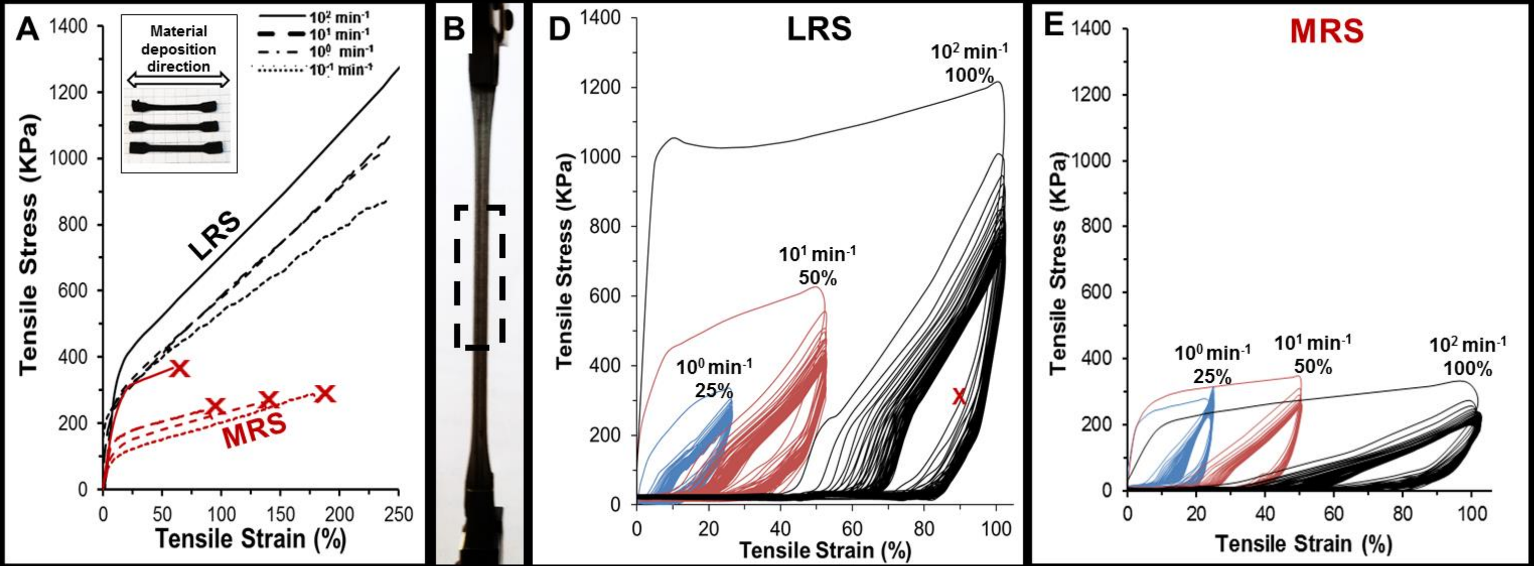
3D-Printed LRS Microstructure

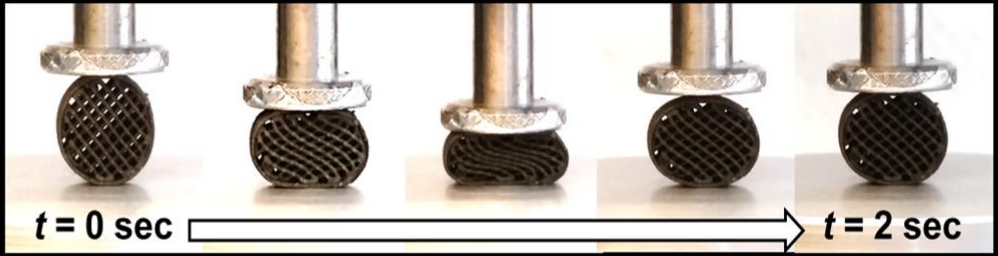


3D-Printed MRS Microstructure



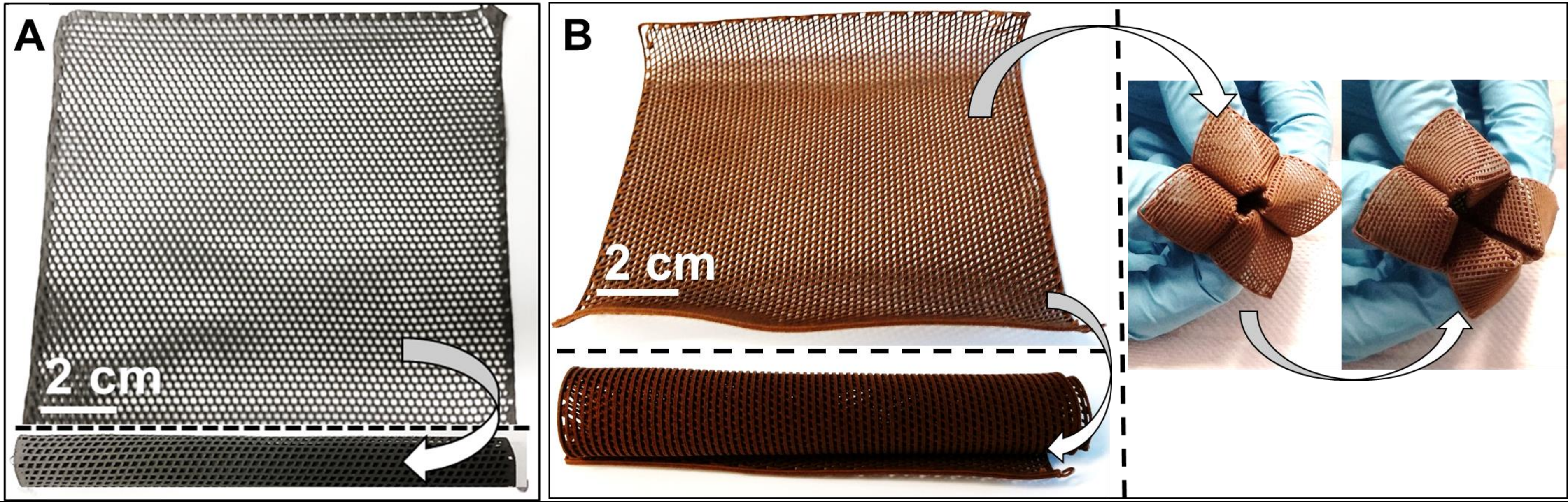
Static and Cyclic Tensile Properties of 3DP LRS and MRS





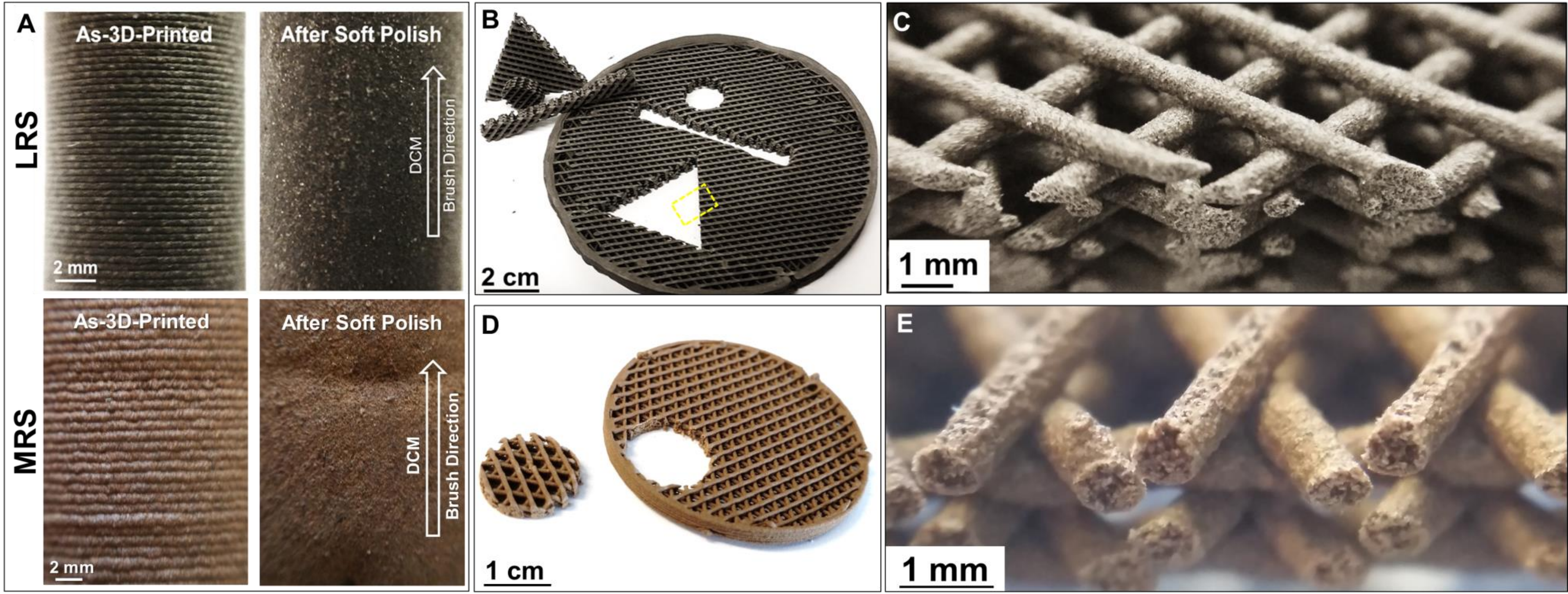
As-3D-Printed LRS and MRS materials have "rubber-like" mechanical properties

Mechanical Manipulation of 3D-Painted LRS and MRS

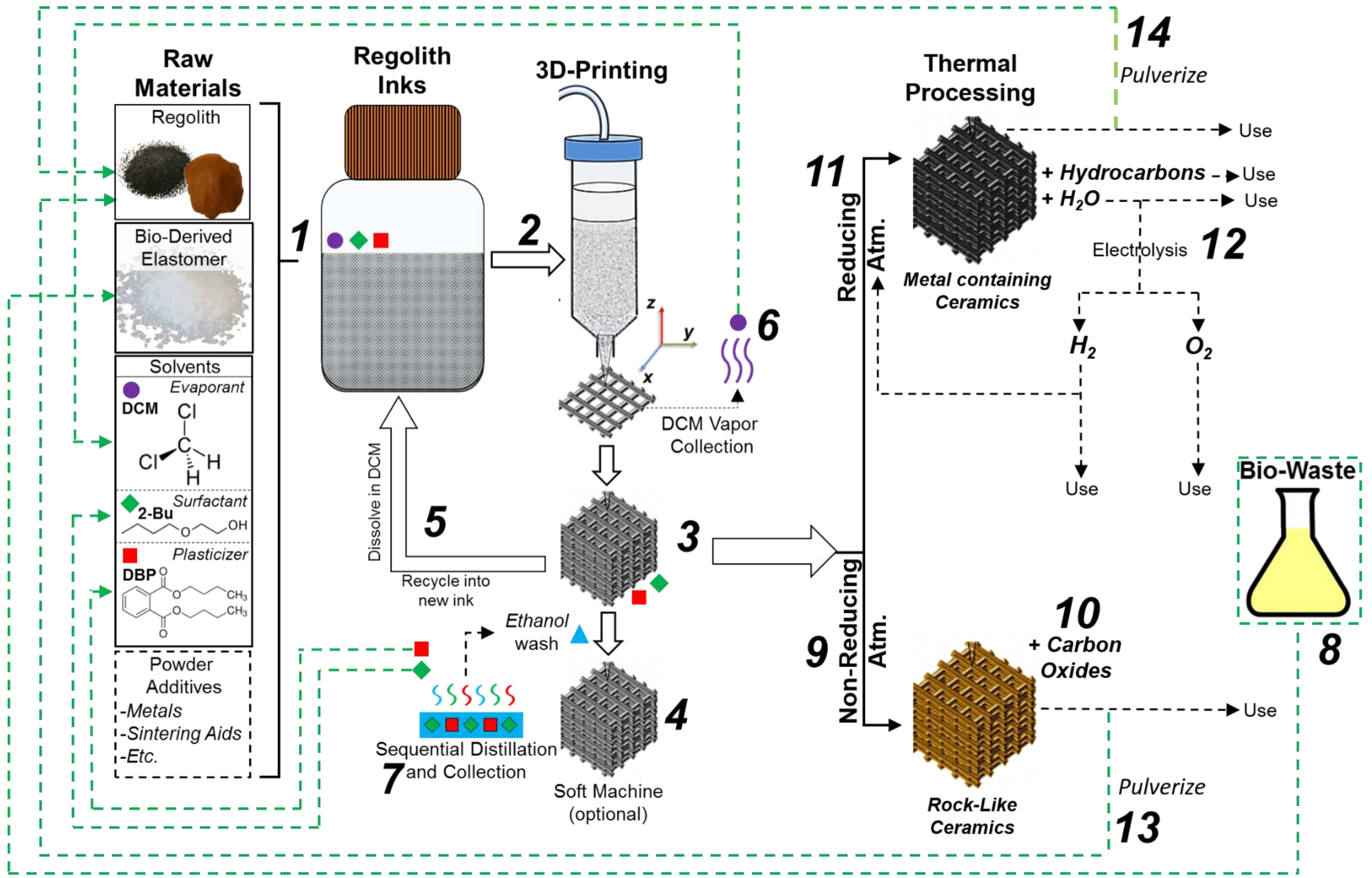


Both 3D-painted LRS and MRS can be elastically and plastically mechanically manipulated

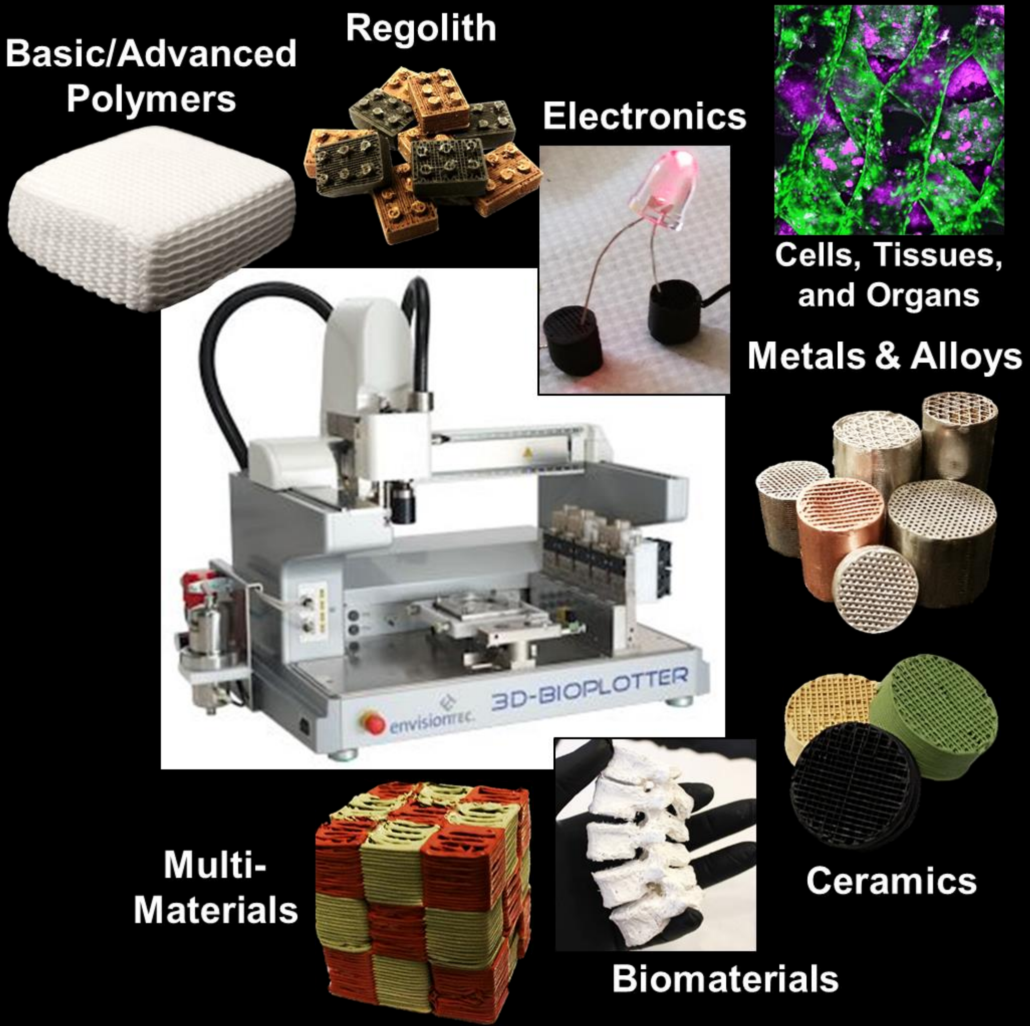
Additional Physical Manipulations of 3D-Painted MRS and LRS



Like all 3D-painted materials, 3DP LRS and MRS can be "polished" with solvent application and also cleanly cut



Raw Materials
Regolith
Bio-Derived Elastomer
Solvents
Evaporant
DCM
Surfactant
2-Bu
Plasticizer
DBP
Powder Additives
-Metals
-Sintering Aids
-Etc.
Regolith Inks
3D-Printing
1
2
3
4
5
6
7
8
9
10
11
12
13
14
DCM Vapor Collection
Dissolve in DCM
Recycle into new ink
Ethanol wash
Sequential Distillation and Collection
Soft Machine (optional)
Thermal Processing
Reducing Atm.
Non-Reducing Atm.
Metal containing Ceramics
Rock-Like Ceramics
+ Hydrocarbons
+ H_2O
Electrolysis
H_2
O_2
Use
+ Carbon Oxides
Pulverize
Bio-Waste



Near-Limitless Materials

On any extrusion-based platform


SHAH TEAM LAB
In Prep.
Fuel Cell Ceramics
3D-Graphene
ACS Nano 9(4). 2015.
(cover)
Hyperelastic
Bone
Science Translational Medicine
(Cover)
ENERGY
MEDICINE
STRUCTURES
Carbon-based Materials
Bioactive Ceramics
Functional & Structural Ceramics
SHAH TEAM LAB
Cell-laden Hydrogels
Metals & Alloys
Natural & Synthetic Polymers
Planetary Soils
Flexible Ceramics
Advanced Structures
In Prep.
Flexible
Bio-Regenerative
Electronics
Advanced Eng. Materials 2016
Advanced Functional Materials 2015.
In Process.
ECM-Derived Materials
Nature Communications 2017.
Advanced Hydrogels
Live Cells and Tissues
Advanced Materials. 27(9). 2015.
Scientific Reports 2017.
Lunar and Martian Simulants
All fabrication performed on a single, extrusion-based 3D-printing instrument

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