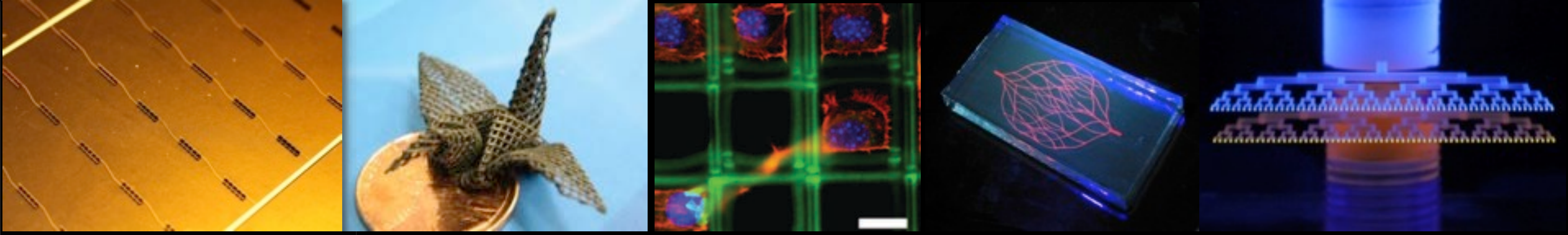


Printing Functional Materials

Jennifer A. Lewis

School of Engineering and Applied Sciences
Wyss Institute for Biologically Inspired Engineering

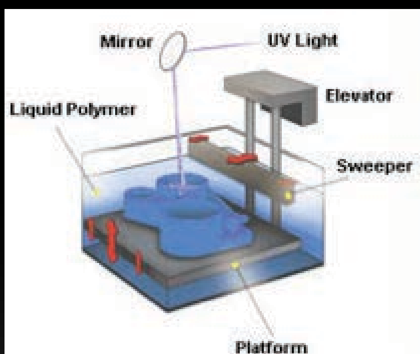
Harvard University

NSF Additive Manufacturing Workshop – 07.11.13

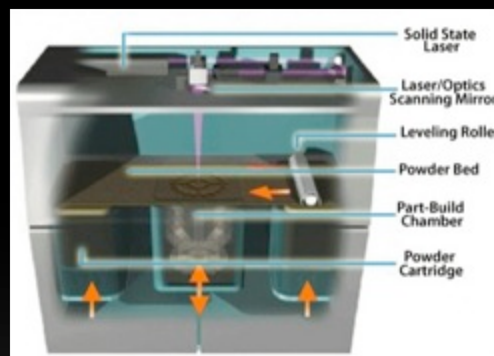
3D Printing – Design, Print, Innovate

Broad range of commercial printers and solidification schemes
(photocuring, ΔT, laser sintering, drying, etc.)

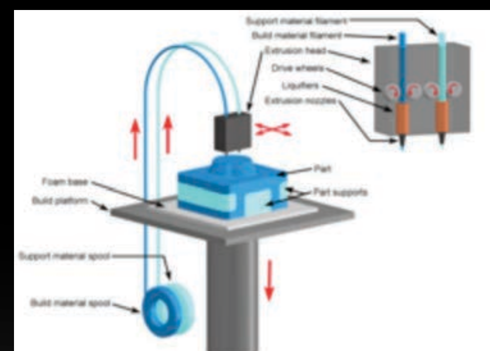
Stereolithography
3D Systems



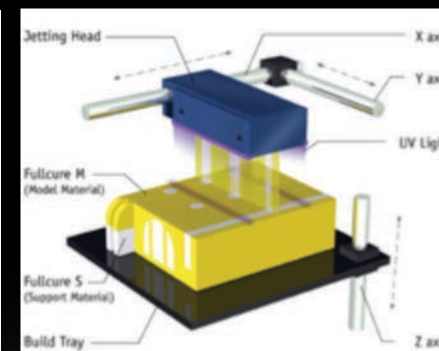
Laser Sintering
3D Systems



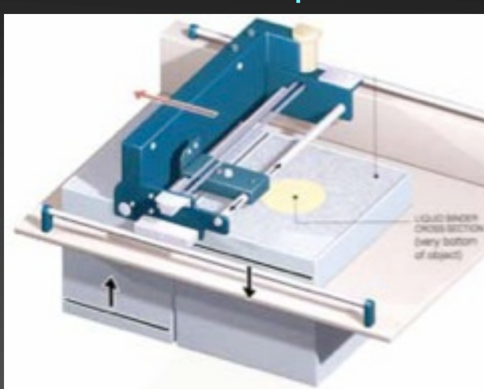
Fused Deposition
Stratasys



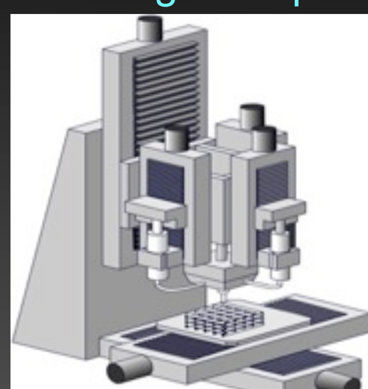
PolyJet Process
Objet



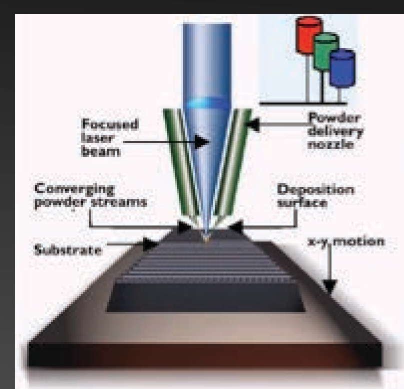
3D Printing
Z Corp



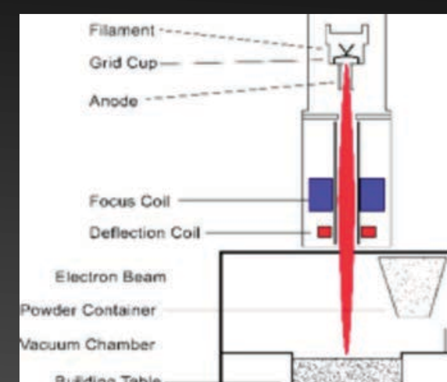
Robocasting
Robocasting Enterprises



Laser Net Shaping
Optomec



Electron Beam Melting
Arcam



3D Printing – Design, Print, Innovate

Broad range of commercial printers and solidification schemes (photocuring, ΔT, laser sintering, drying, etc.)

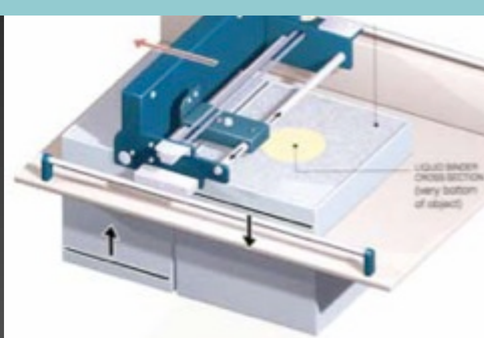
Stereolithography	Laser Sintering	Fused Deposition	PolyJet Process
3D Systems	3D Systems	Stratasys	Objet

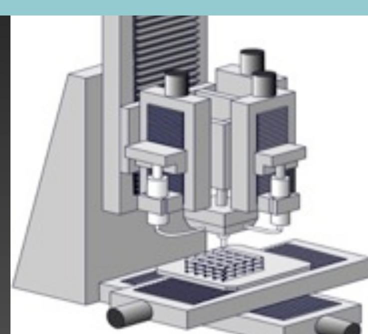
Most 3D printing methods lack one or more of the following attributes:

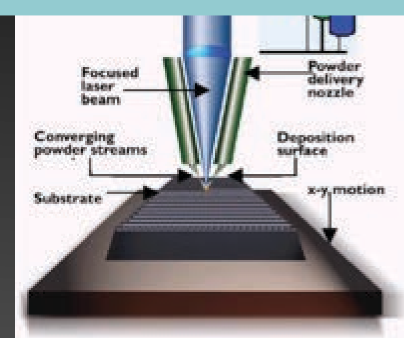
(1) Materials flexibility

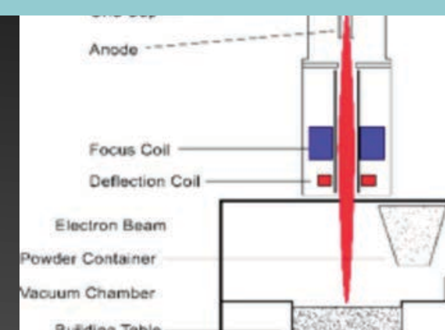
(2) Ability to pattern fine features (< 100 μm)

(3) High throughput









Several advances needed for 3D printing of high performance, functional materials

"Before this personal manufacturing revolution can take place, though, researchers will need to develop a broader array of robust printing materials…"

"… rapidly growing market, $1 B sales…
about 70% of market is prototyping"

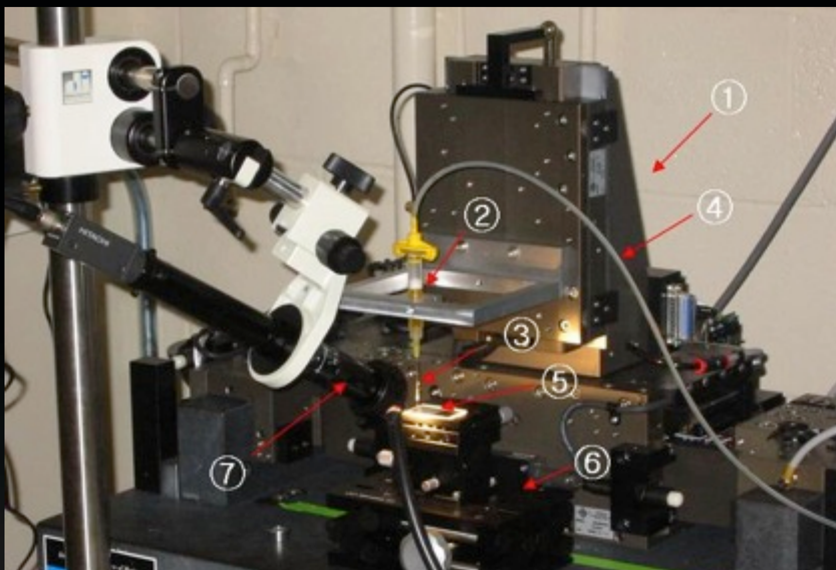
Chemical & Engineering News, Nov 14, 2011 issue

Our research focus

- Broaden materials palette for 3DP
- Integration of multiple materials
- Digitally specify form <u>and</u> function
- Improve feature resolution by 100x
- Improve throughput by 100x

… expedite transformation from rapid prototyping to manufacturing of functional materials

Custom stages designed for 3D printing



Moderate Area, High Precision

10x10x5 cm^3 ± 50 nm
V = 0.1 -10 mm/s

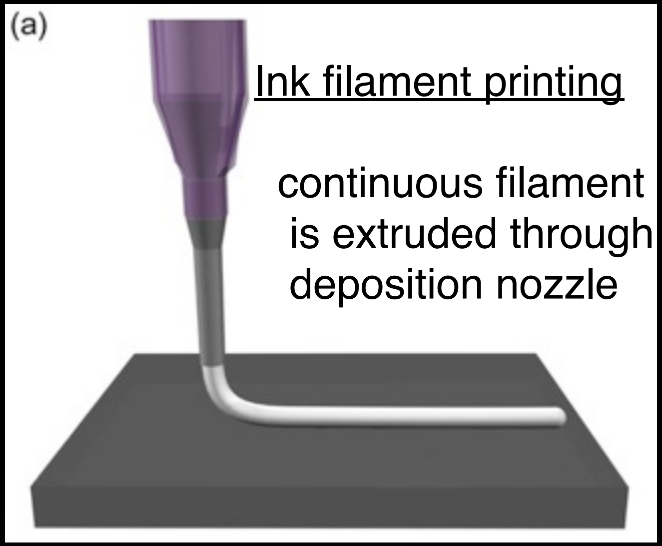
Large Area, High Speed Stage

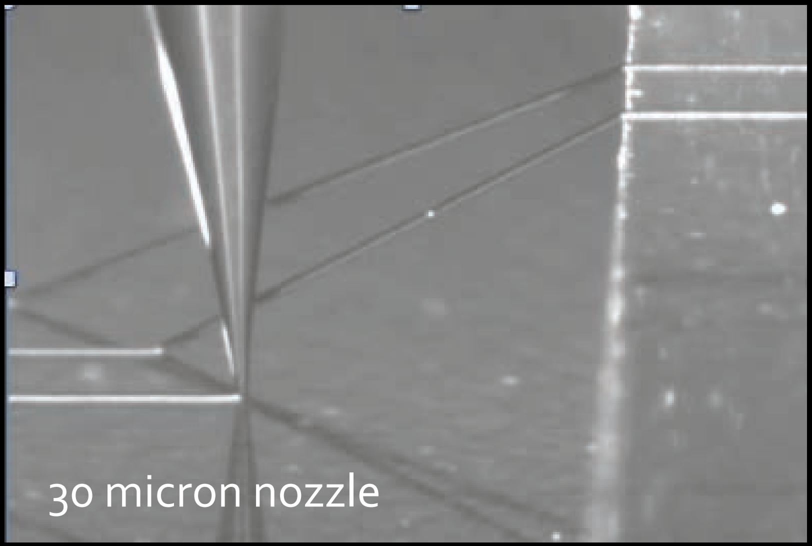
$1 m^2$x10 cm ± 5 μm
V = 1 -1000 mm/s

High precision, large area,
and high speed stages

+ integrating multiple 3D printheads

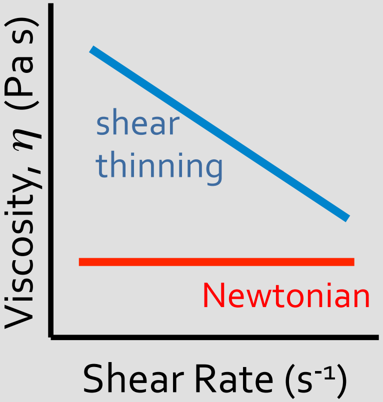
Printing ink filaments (in and out of plane)

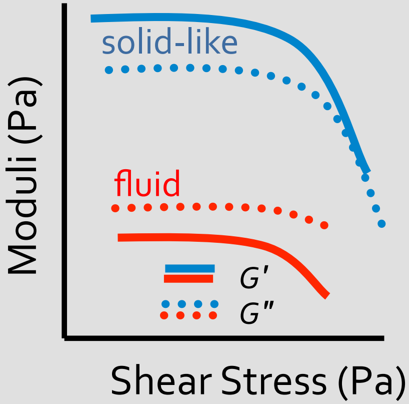




Desired Ink Rheology:

- Shear thinning behavior facilitates flow through fine nozzles without clogging
- Viscoelastic behavior enables printing of self-supporting (spanning) features





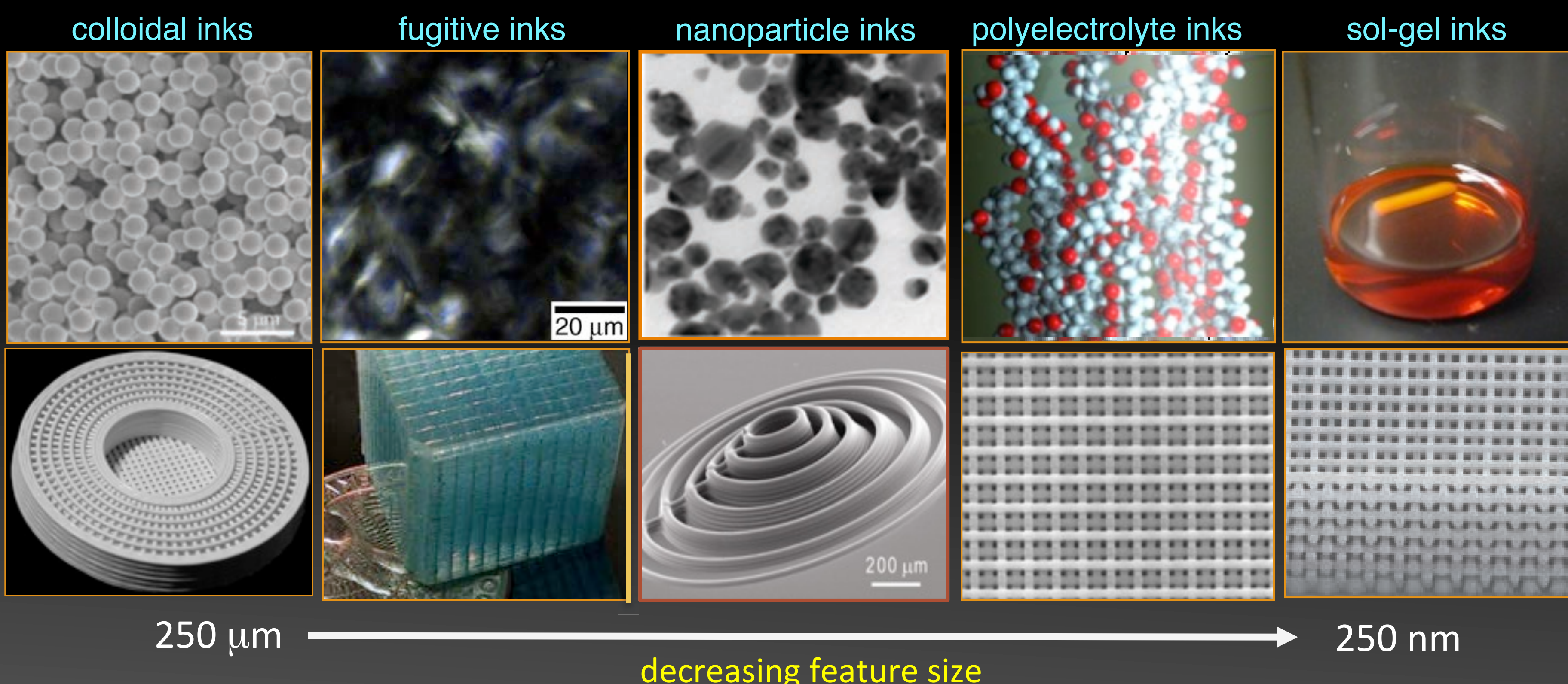
Filamentary printing

Unable to retain filamentary shape

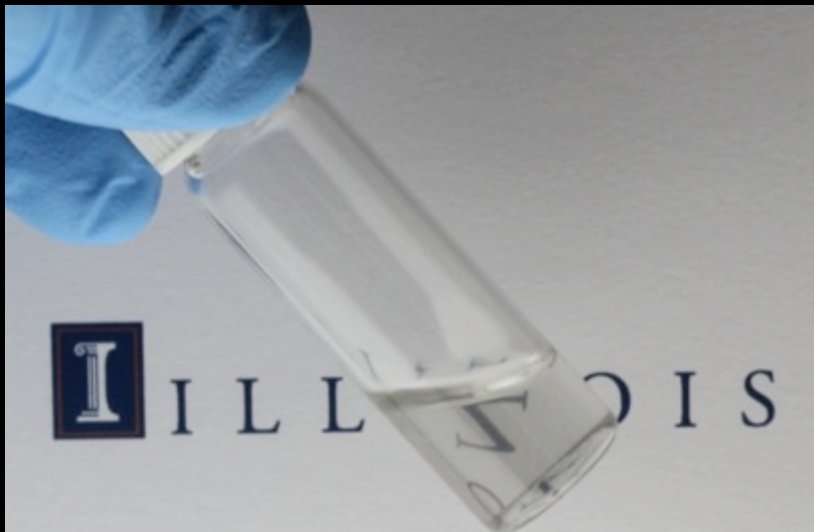
Viscoelastic inks designed for 3D printing

Ink design and deposition

- ink must flow through nozzle without jamming
- ink filaments must form high integrity interfaces
- ink must solidify rapidly (via gelation, coagulation, or evaporation)
- concentrated inks minimize shrinkage during drying

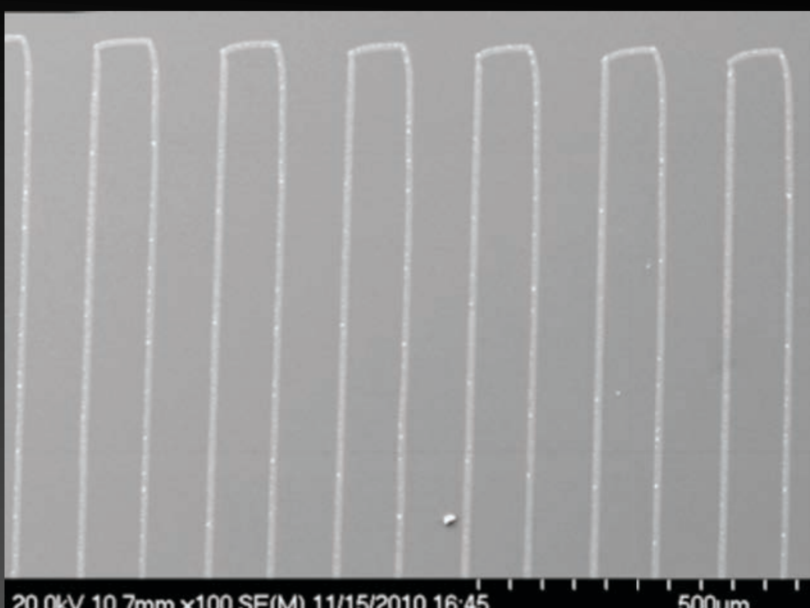


Reactive silver inks for integrated electronics



Walker, Lewis *JACS* (2012); Patent filed

* 90% bulk conductivity at 100°C



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9 Materials That Will Change the Future of Manufacturing [Slide Show]

Researchers are developing cutting-edge foams, coatings, metals and other substances to make our homes, vehicles and gadgets more energy efficient and environmentally friendly

By Steven Ashley and Larry Greenemeier | April 22, 2013 | 4

Share Email 2 of 9

Article: 9 Materials That Will Change the Future of Manufacturing [Slide Show] »

April 22, 2013

ELECTRIC INK: Quantum-electronic magic can make strange but useful semiconductors that are insulators on the inside and conductors on the surface. The bulk of the material acts as an insulator that blocks electron flow whereas the surface is a very good, metal-like conductor that allows electrons to travel freely at almost light-speed, unaffected by impurities that normally hinder electron motion through materials. Metal-free conductive inks will play a role in making printed electronic materials used in display screens, sensors and batteries. University of Illinois researchers, for example, have created a silver-based electric ink that leaves a trail of conductive material when it evaporates. The new formulation is easier to make than conventional electronic inks, adheres to many materials and can be printed at a lower temperature using a simple desktop device. [Less] [Link to this slide]

Courtesy of University of Illinois / S. Brett Walker

electroninks

Silver particle inks for integrated electronics

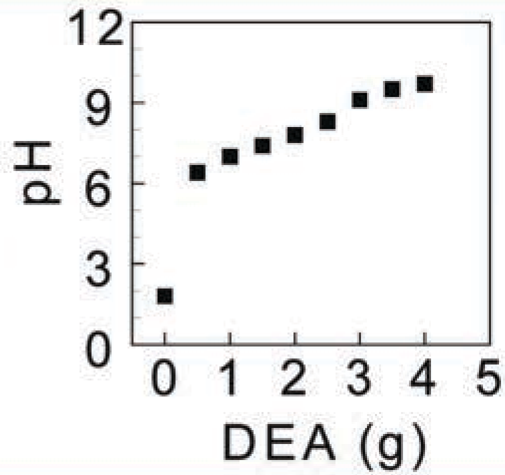
Starting Materials

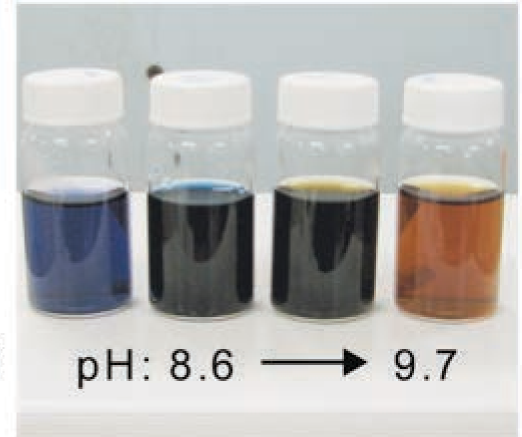
Silver source : $AgNO_3$

Stabilizer : Poly(acrylic acid), PAA

Reductant : Diethanolamine, DEA

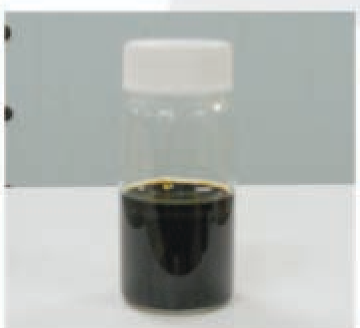
Solvent : Deionized H_2O

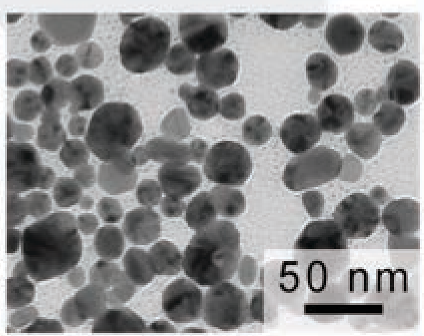




Particle Growth

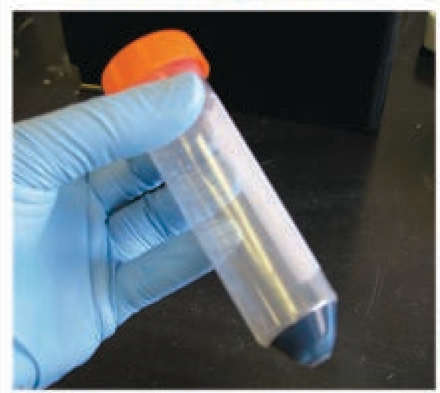
Sonication (60 °C, ~2 h)





20 nm average , 5 – 50 nm distribution

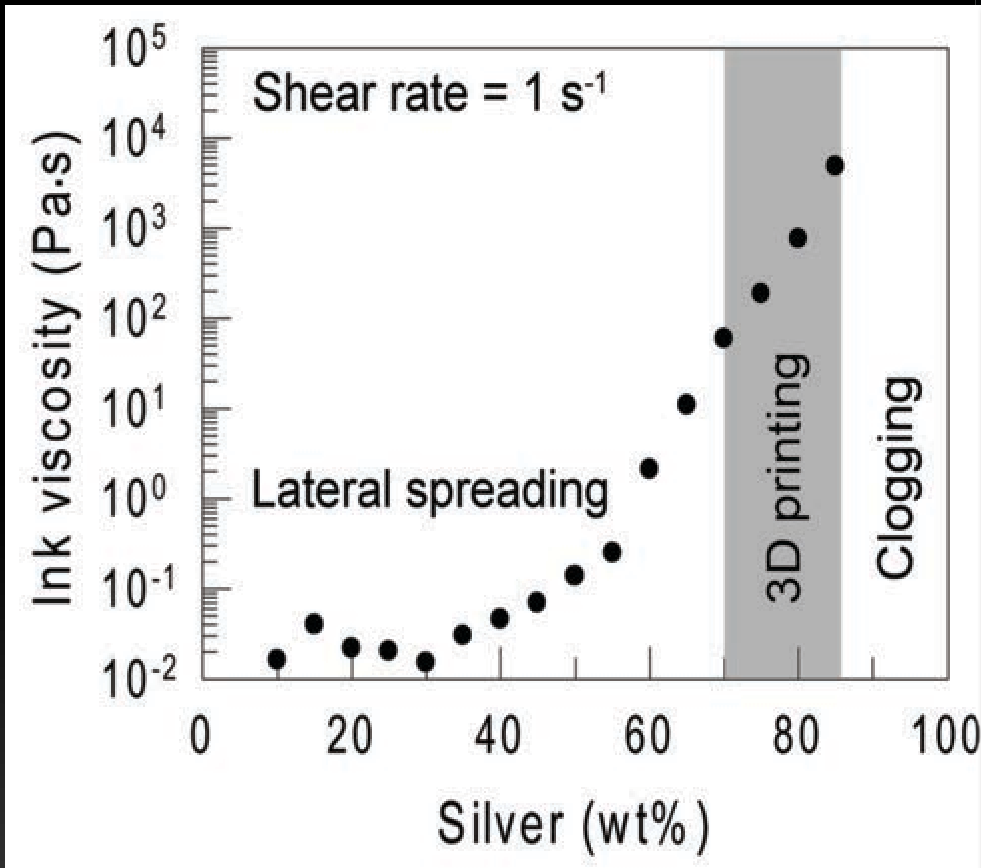
Phase Separation Centrifugation

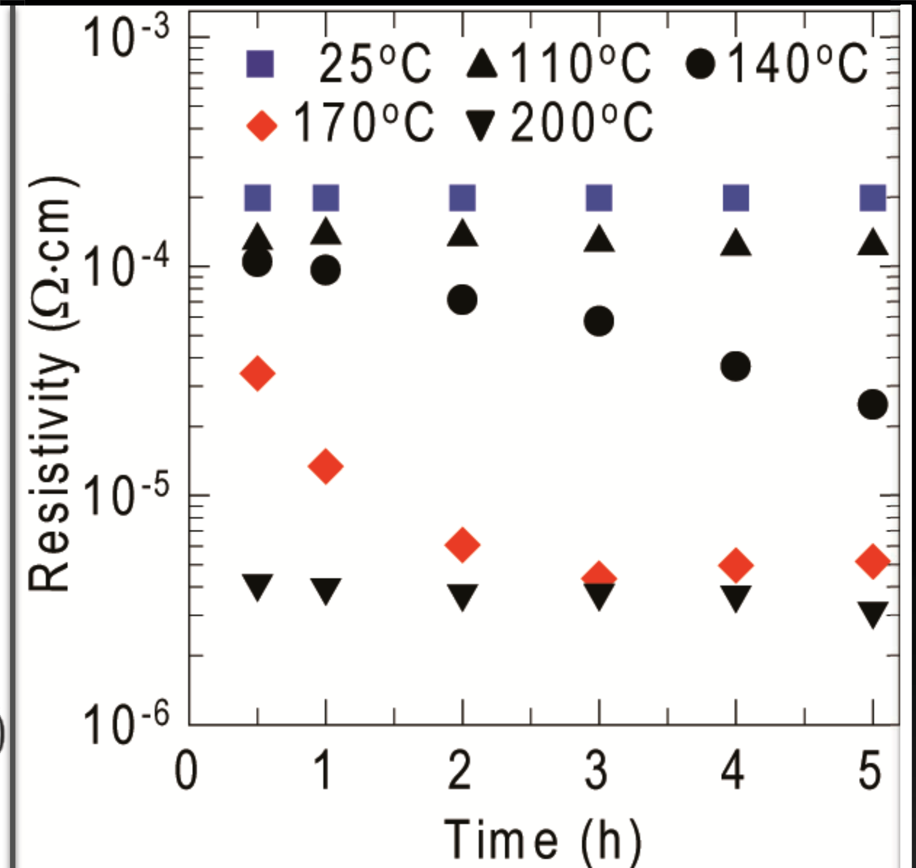


Homogenization Add Humectant

Ahn, Duoss, Nuzzo, Rogers, Lewis, et al., *Science* (2009); Ahn, Duoss, and Lewis, US-Patent 7,922,939

Silver particle inks for printed electronics

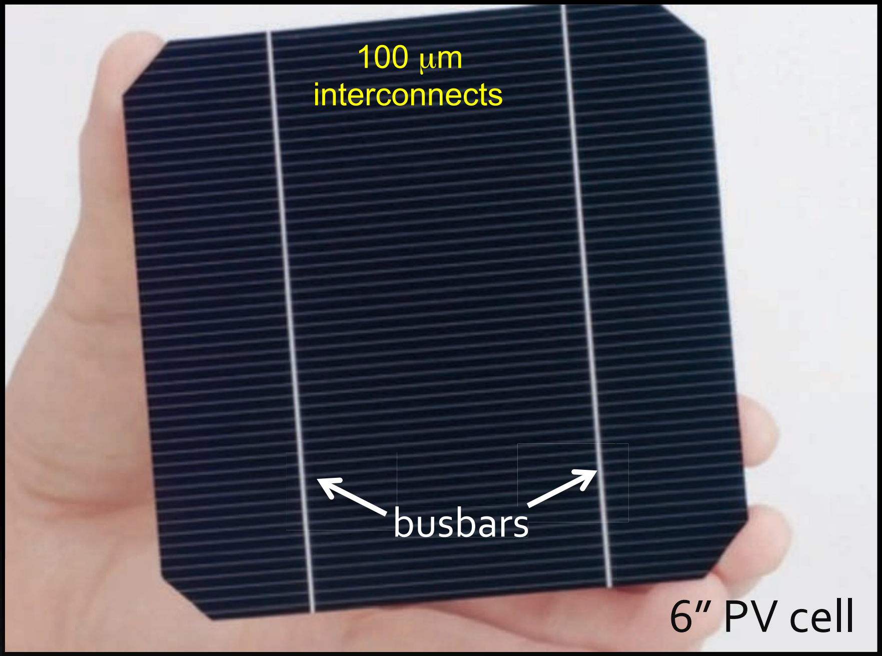




Silver inks are highly conductive as-printed

Ahn, Duoss, Nuzzo, Rogers, Lewis, et al., *Science* (2009); Ahn, Duoss, and Lewis, US-Patent 7,922,939
Russo et al., Advanced Materials (2011)

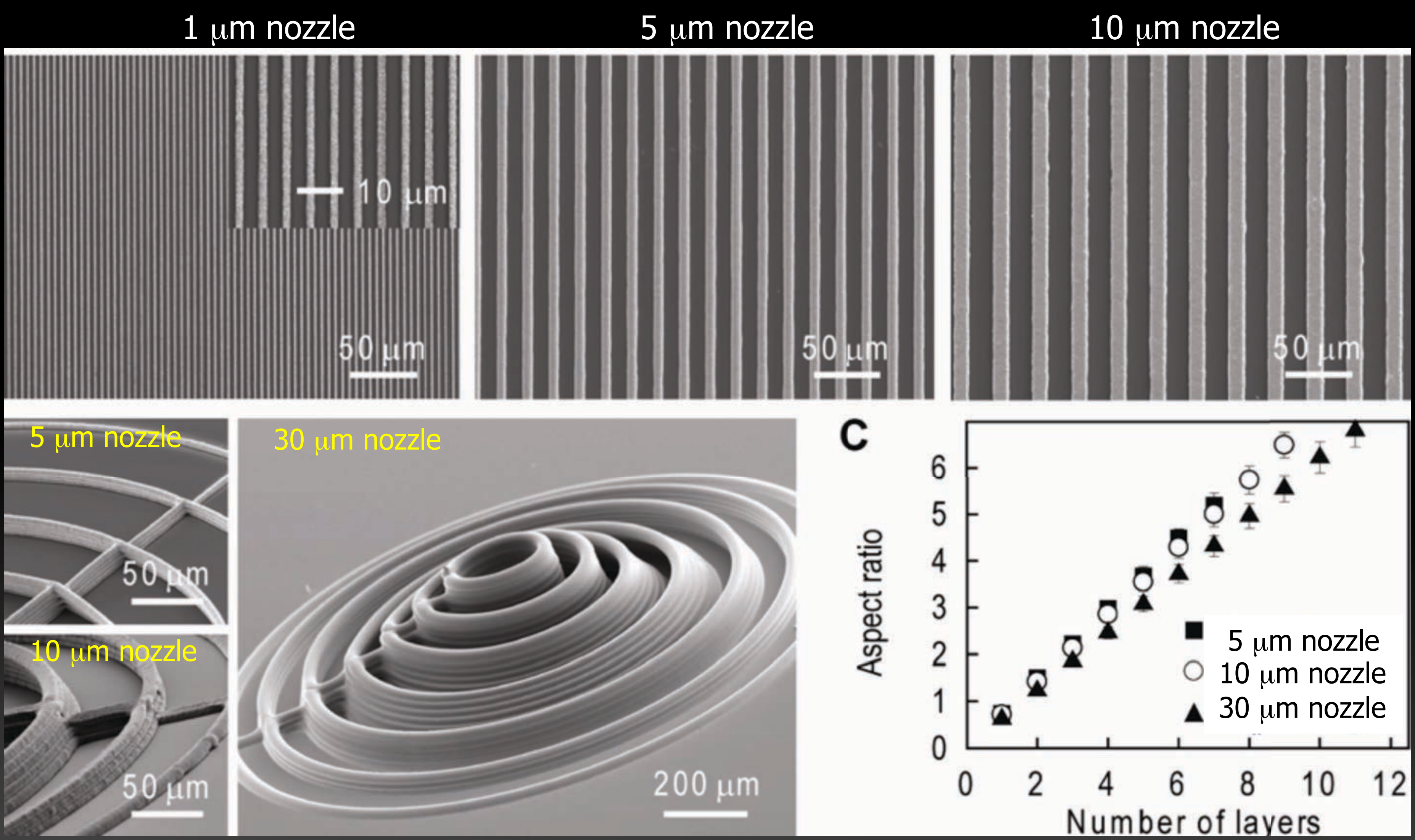
Solar panels - present design



Rigid, costly, active materials* occupy large area

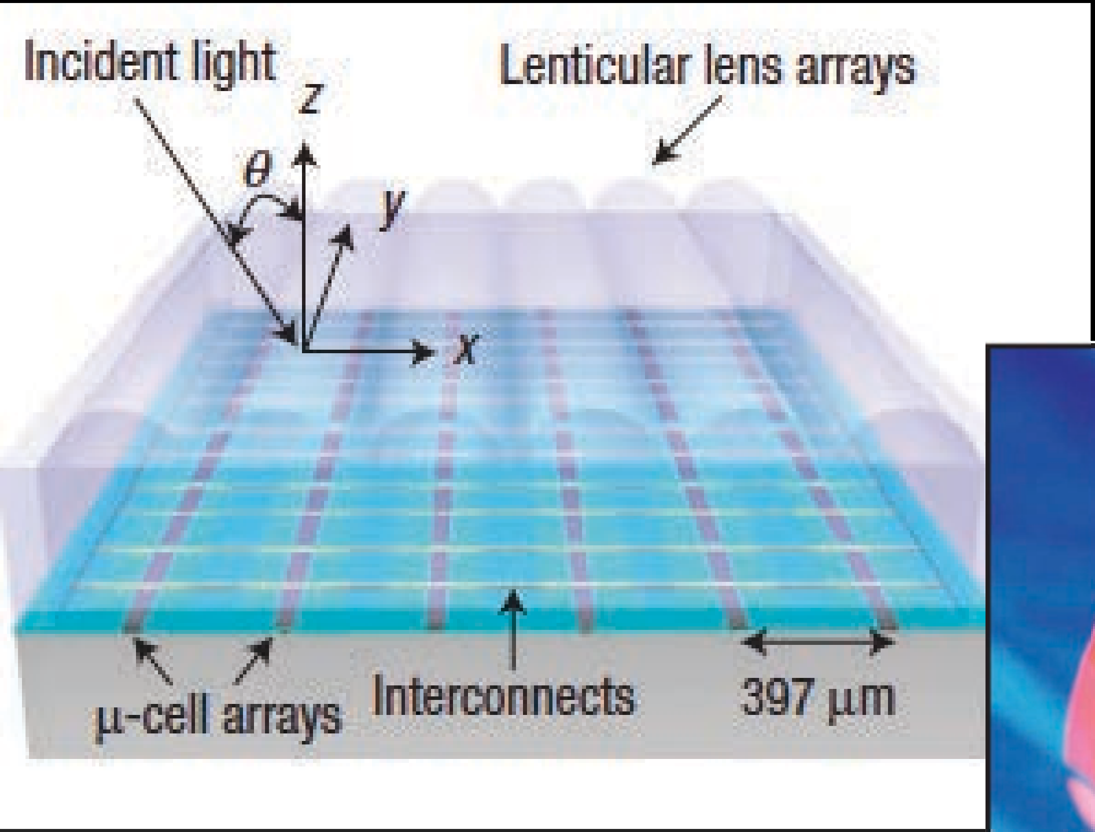
*silicon PV cells and silver interconnects

Printing High Aspect Ratio Silver Microelectrodes

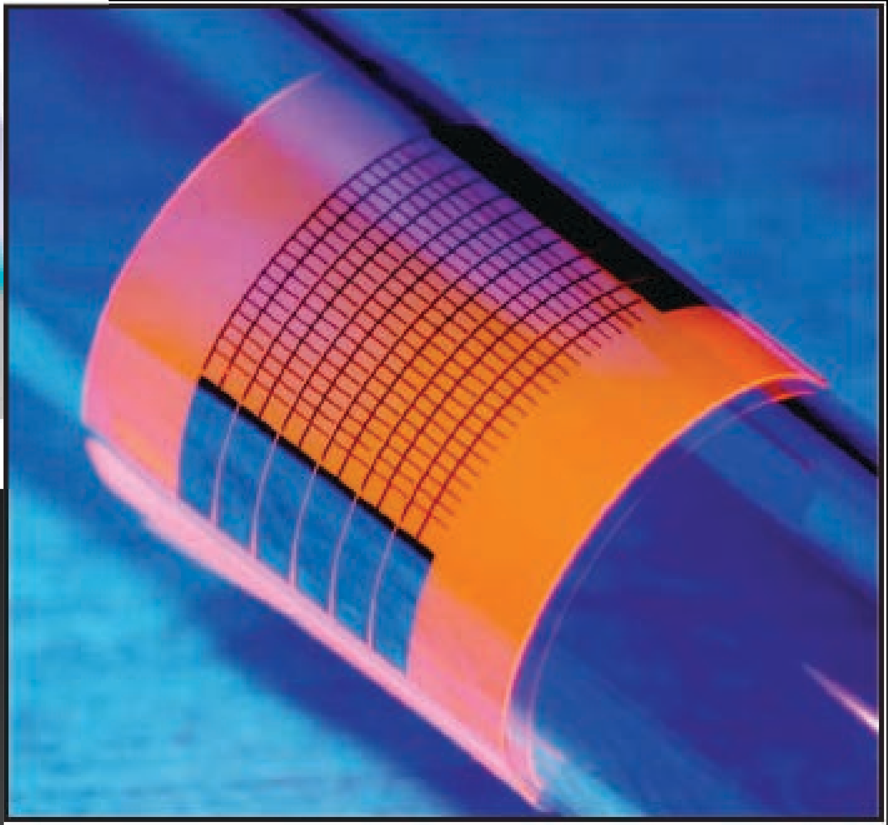


Ahn, Duoss, Nuzzo, Rogers, Lewis et al. *Science* (2009).
Ahn, Duoss, and Lewis, US-Patent 7,922,939

Flexible photovoltaics



Example:
Si microcells +
Luminescent layer
(UV-curable and organic dye)

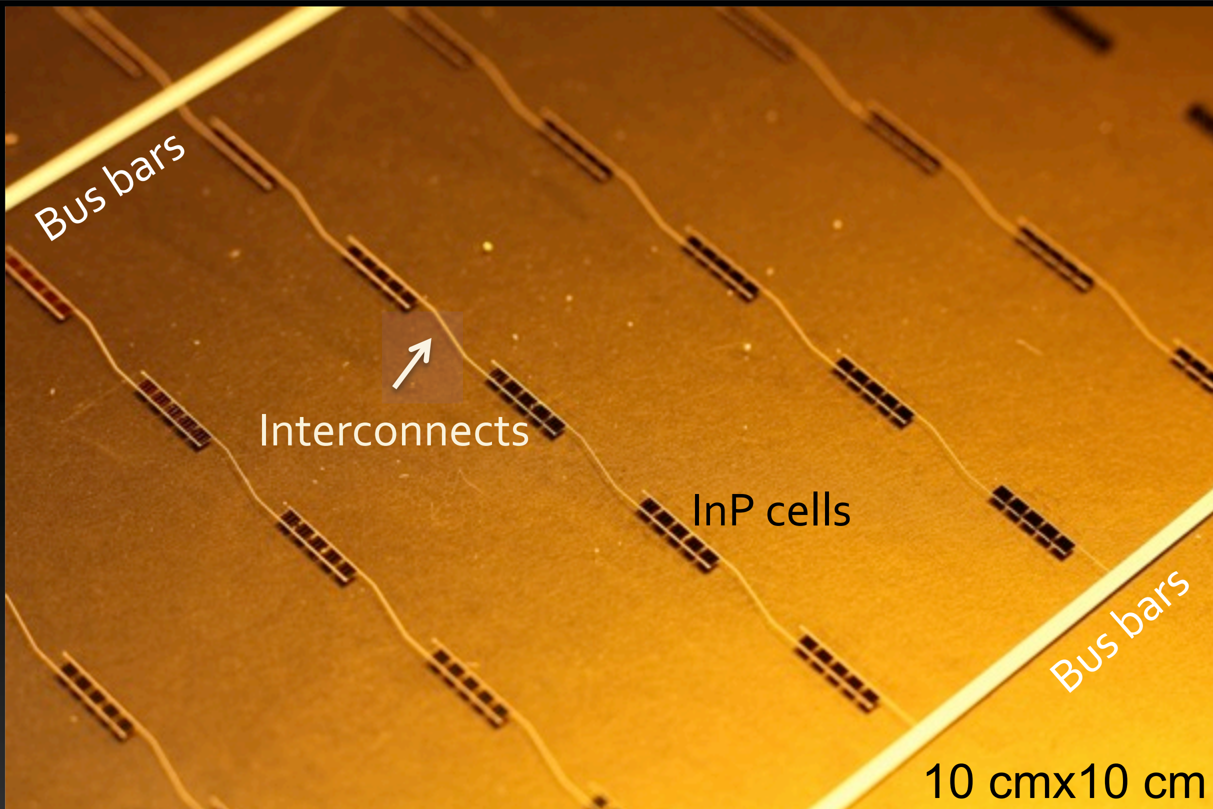


Vast reduction in active materials used

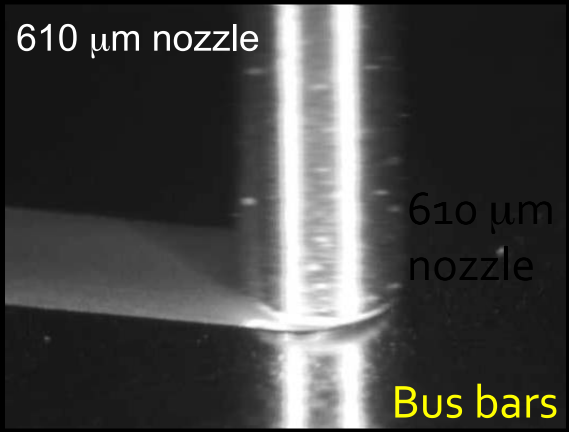
Printable microcells & interconnects combined with concentrator optics

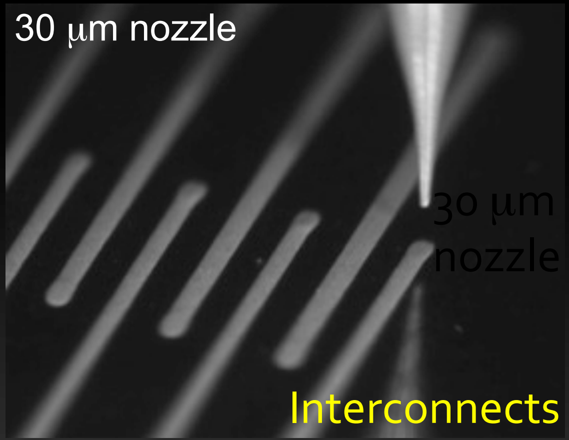
Rogers, Nuzzo,et al, *Nature Comm.* (2011).

Printing interconnects and bus bars



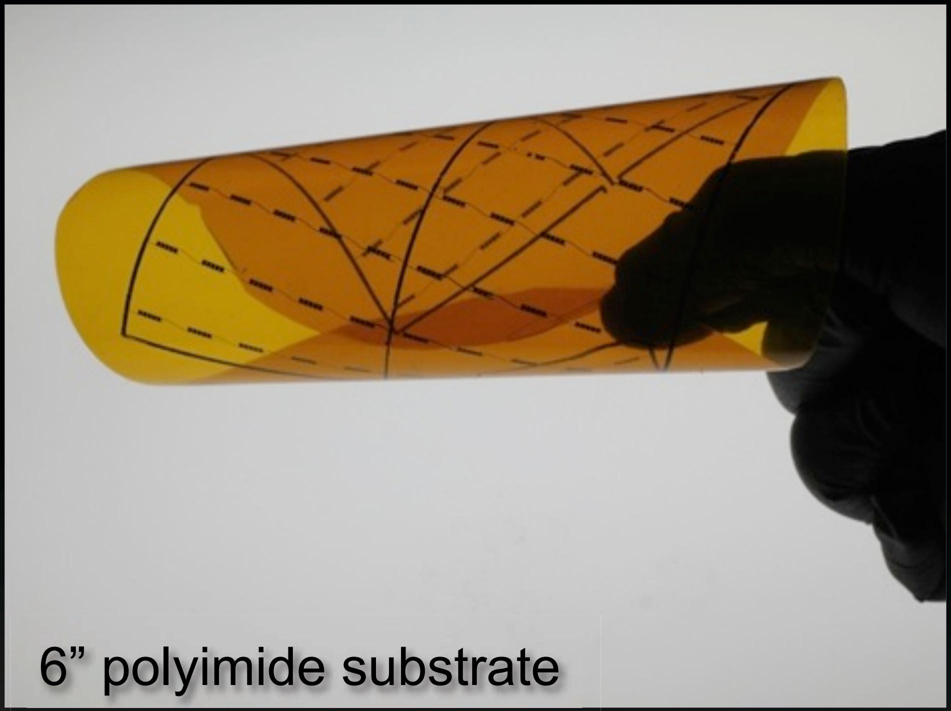
Sparse array of PV cells; finer interconnects



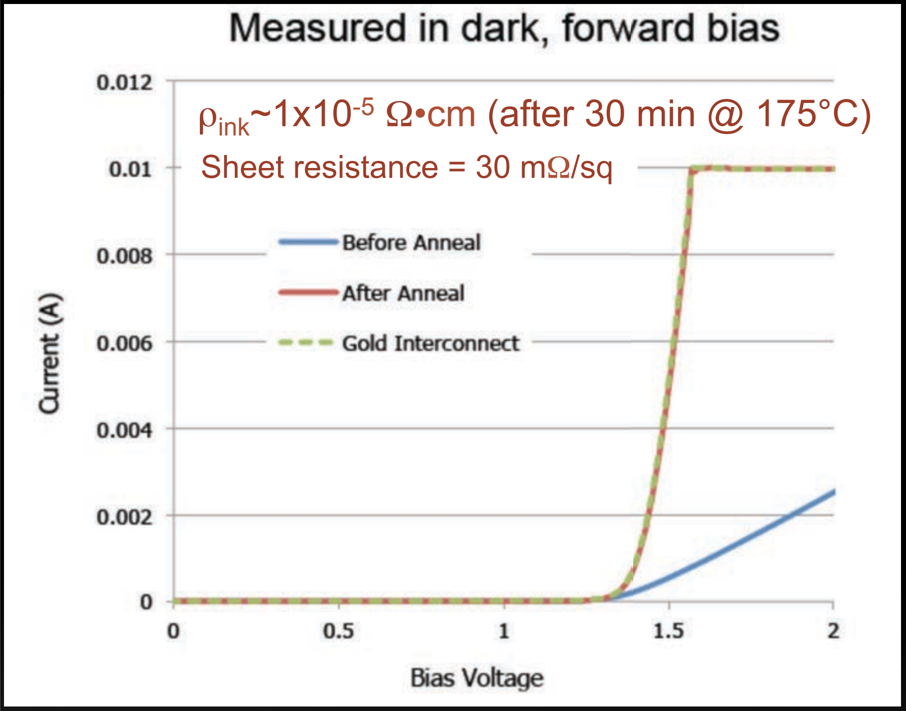


In collaboration with Semprius and SAIC

Flexible concentrator photovoltaics



6” polyimide substrate

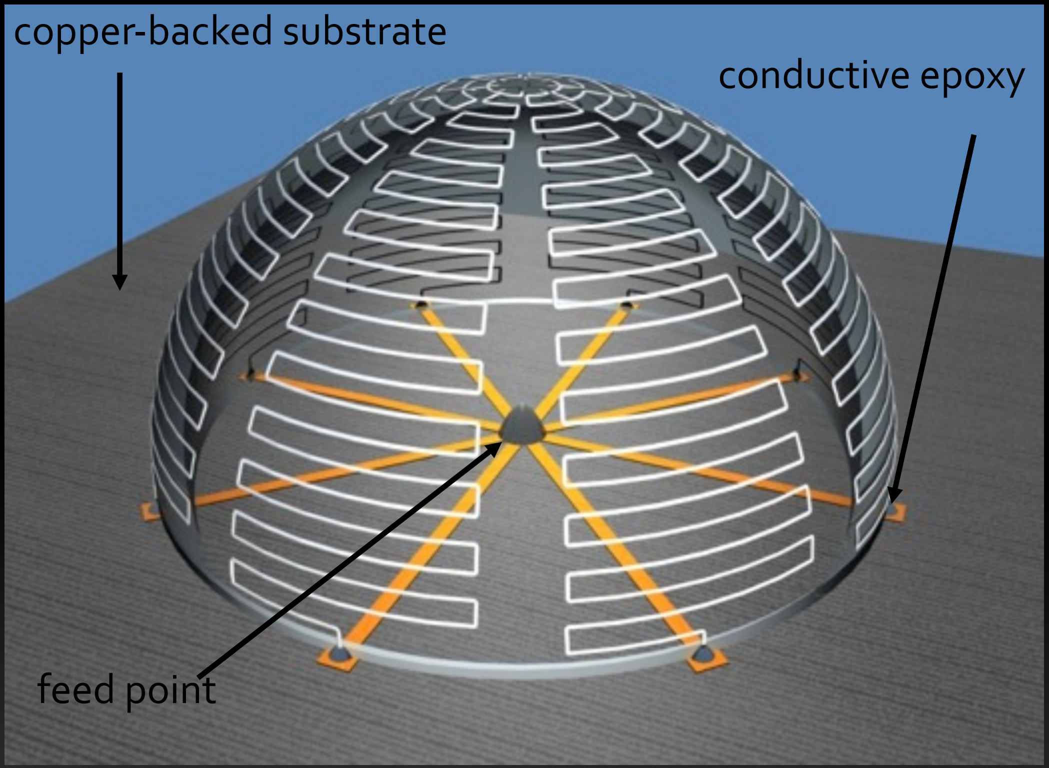


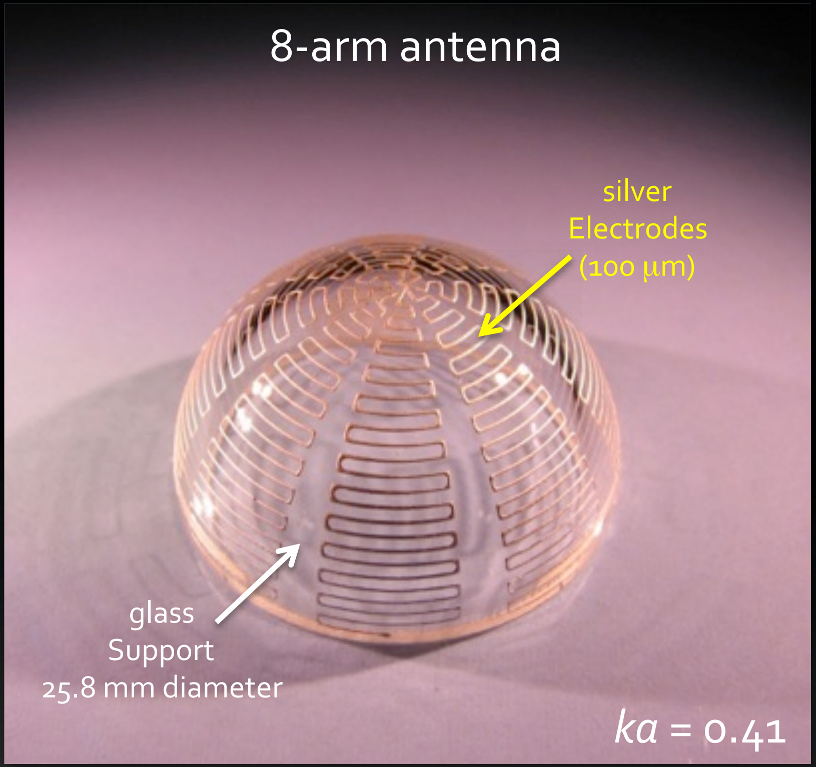
Printed interconnects are highly flexible and can withstand repeated bending (1000’s cycles) without performance loss

Printed interconnects exhibit excellent I-V response

In collaboration with Semprius and SAIC

Conformal printing of electrically small antennas





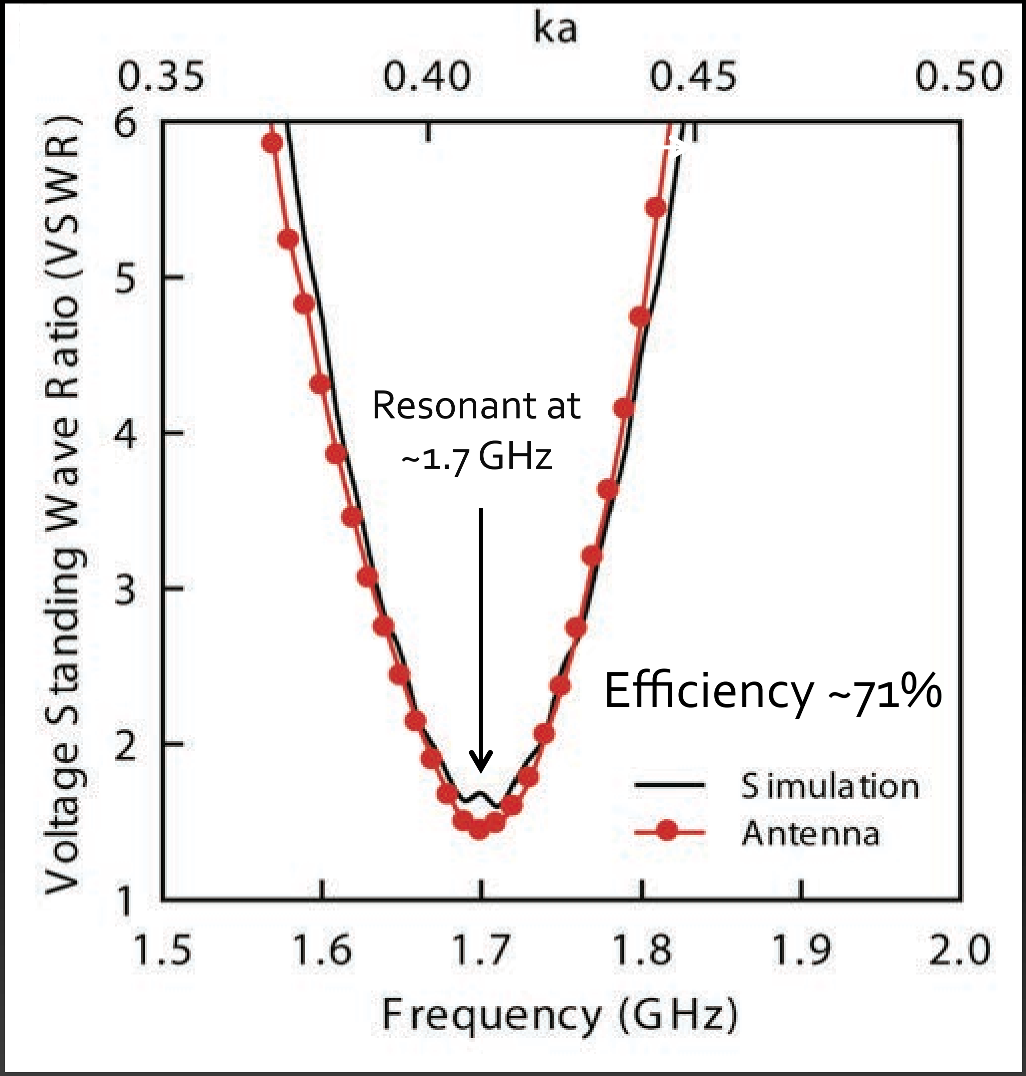
with Bernhard group (ECE @ Illinois)

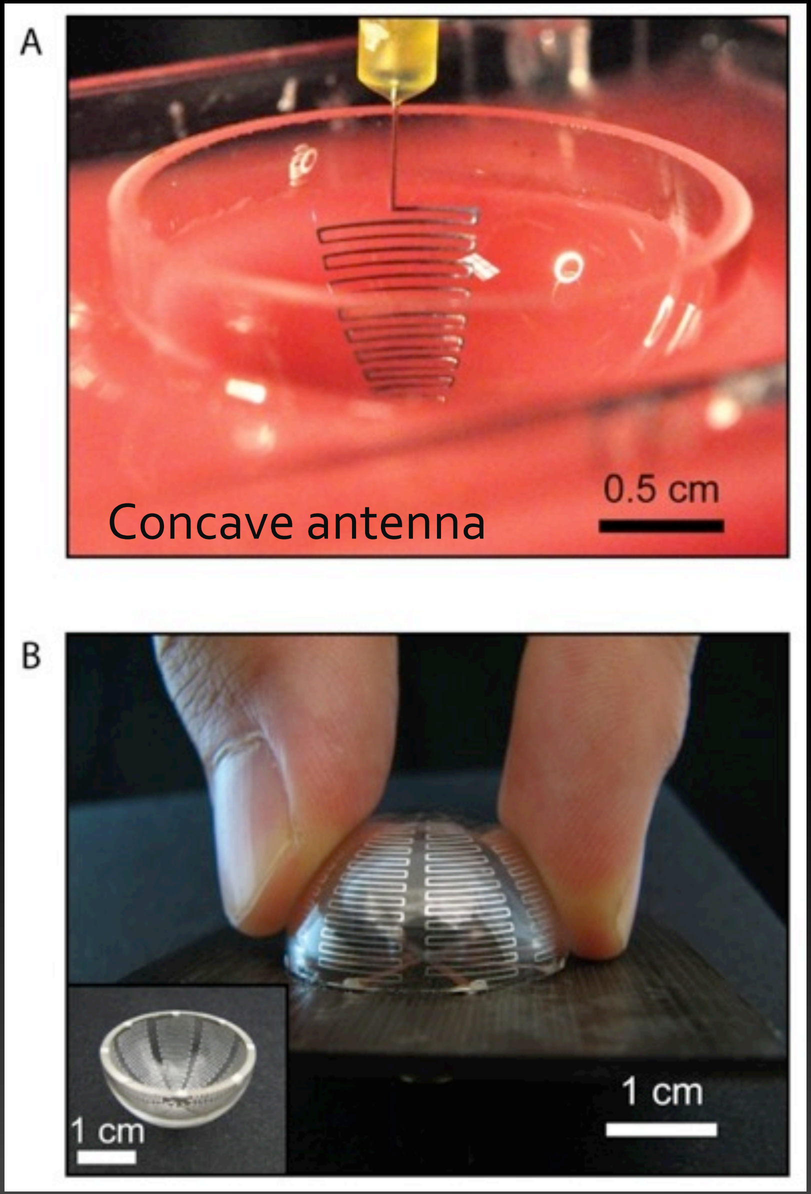
$$k = \frac{2\pi}{\lambda_0}$$

ka < 0.5 indicates an electrically small antenna (ESA)
i.e., $a < \lambda_0/4\pi$

Adams, Duoss, Malkowski, Ahn, Nuzzo, Bernhard, Lewis, *Advanced Materials* (2011)

Performance characteristics



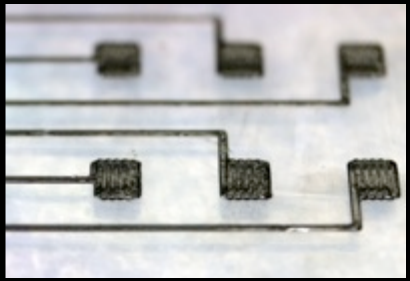


VSWR: a measure of signal reflected at component junctions
Ideally, VSWR = 1 (no reflected power, no mismatch loss)

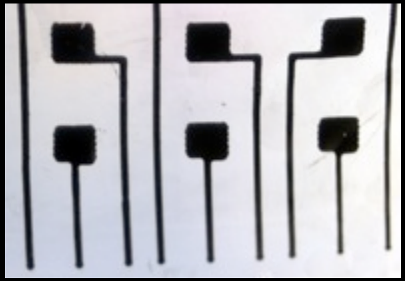
Adams, Duoss, Malkowski, Ahn, Nuzzo, Bernhard, Lewis, *Advanced Materials* (2011)

Embedded Electronics (carbon ink printed in polymer matrix)

400 µm nozzle



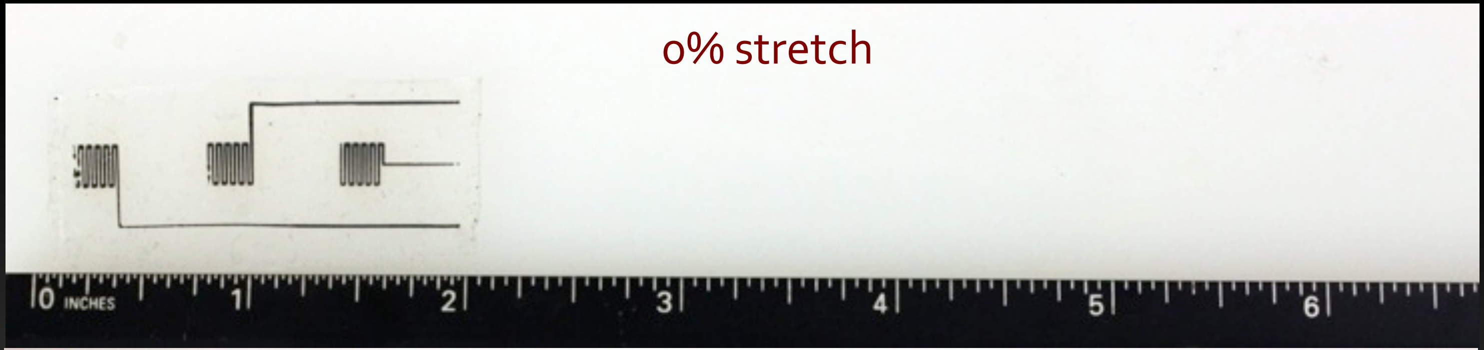
As printed



After encapsulation

---

200 µm nozzle



Muth

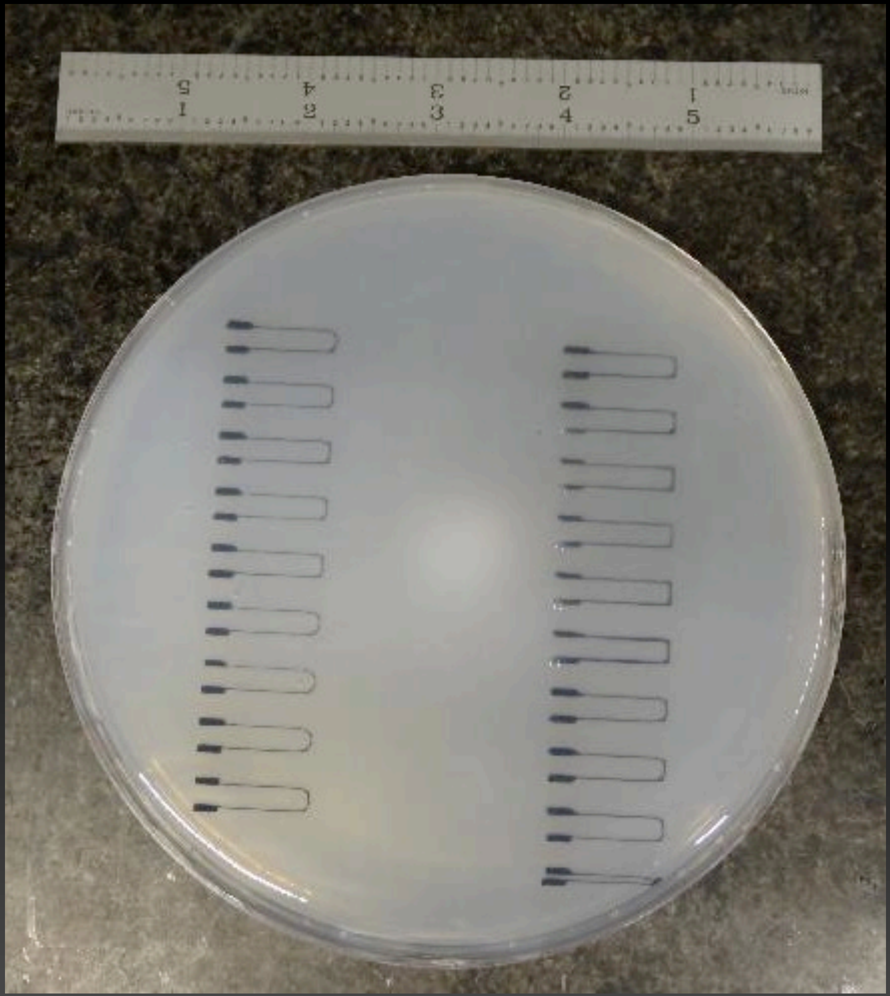
Kolesky

with the Wood group

Embedded Electronics (carbon ink printed in polymer matrix)

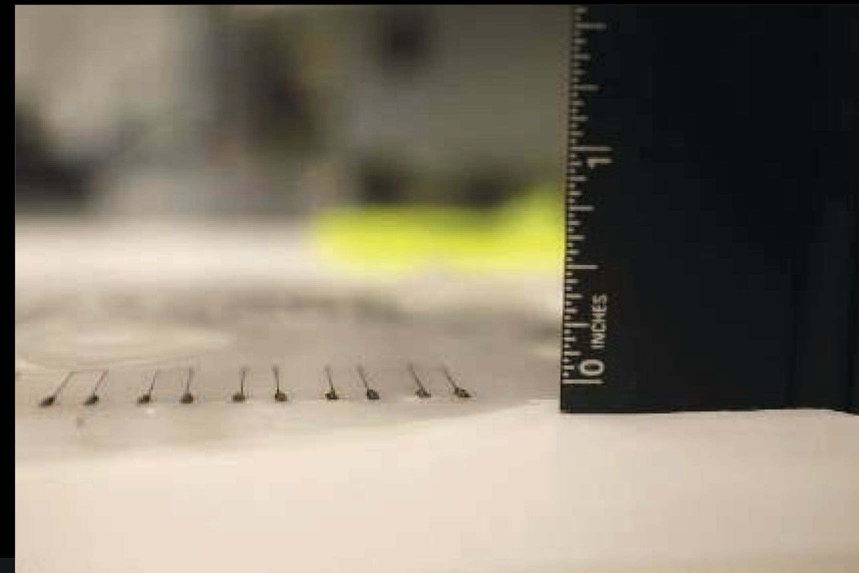
Strain Gage
Length = 20 mm

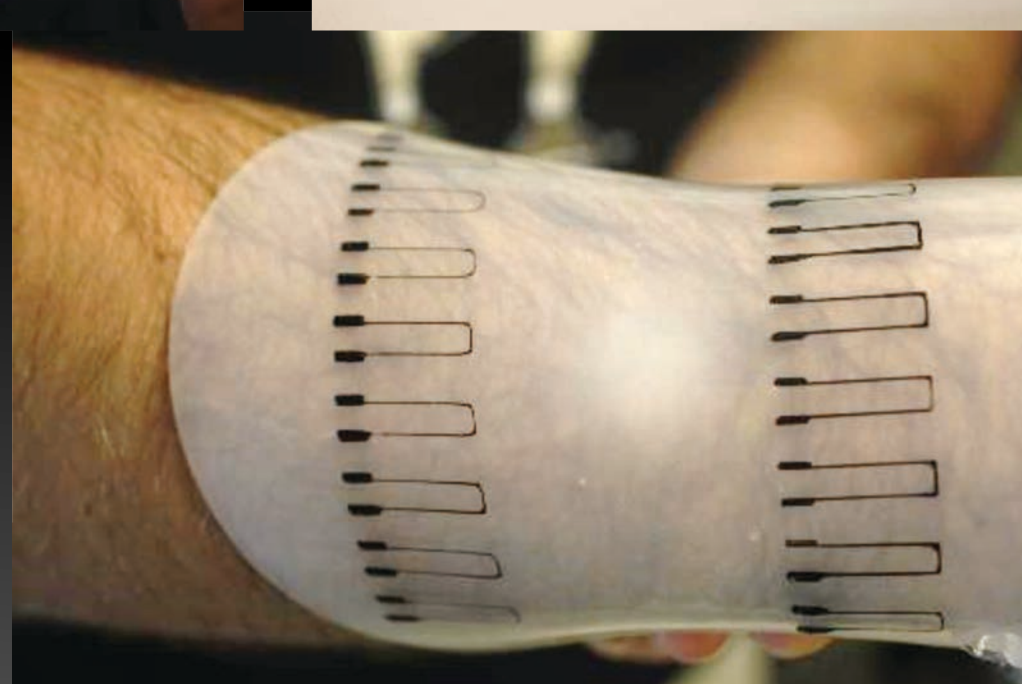
All printed sequentially in 1mm thick EcoFlex reservoir



with the Wood group

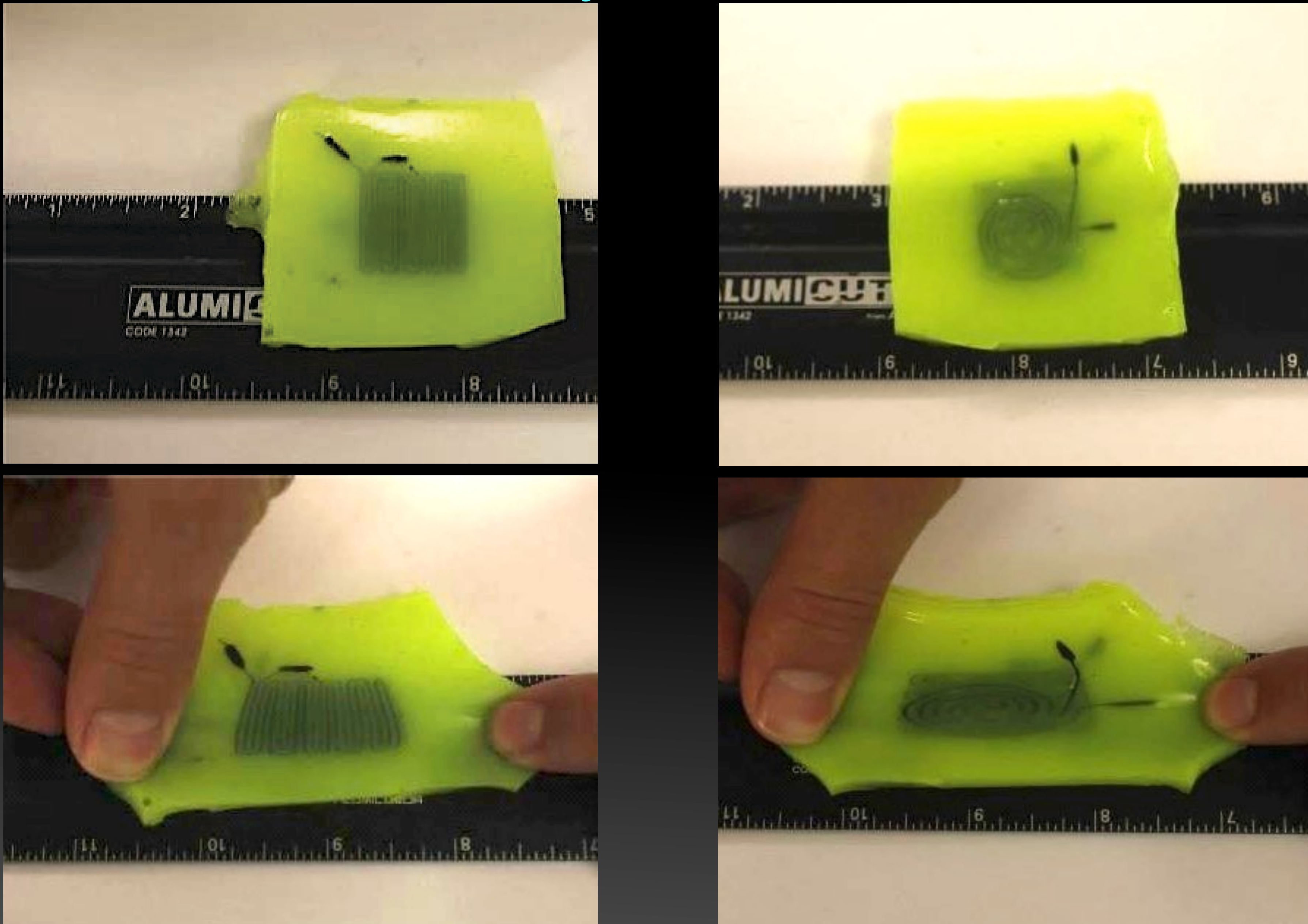
3D Printed of Strain Gage Arrays





with the Wood group

Printed Three-Layer Stretchable Sensors



with the Wood group

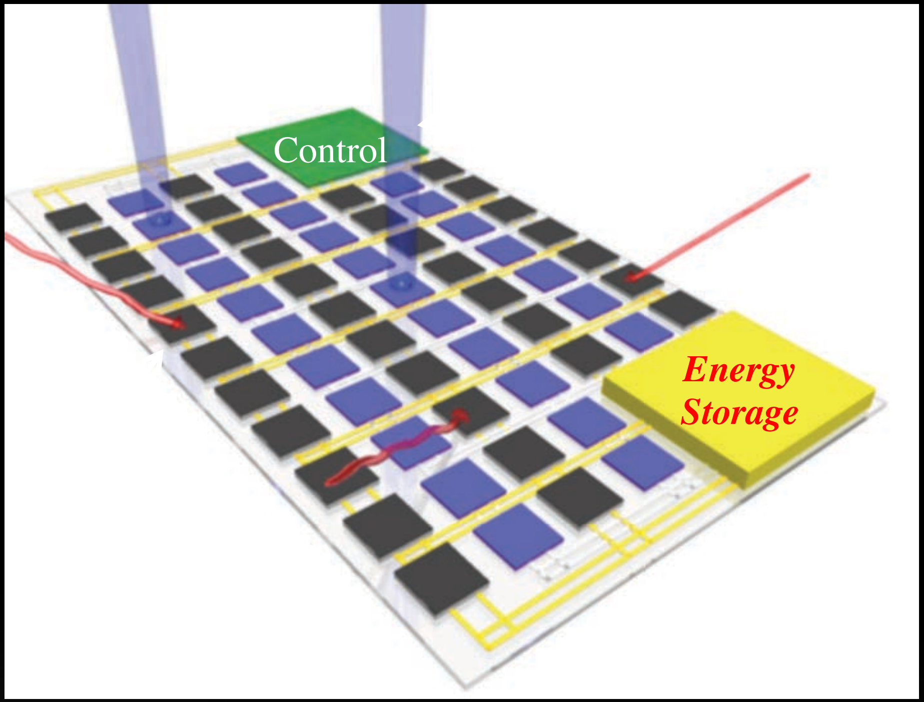
Aim: Print Microbatteries w/ High Power & Energy Density

For autonomous devices that:

1. Harvest energy
   - photovoltaic
   - thermoelectric
   - piezoelectric…

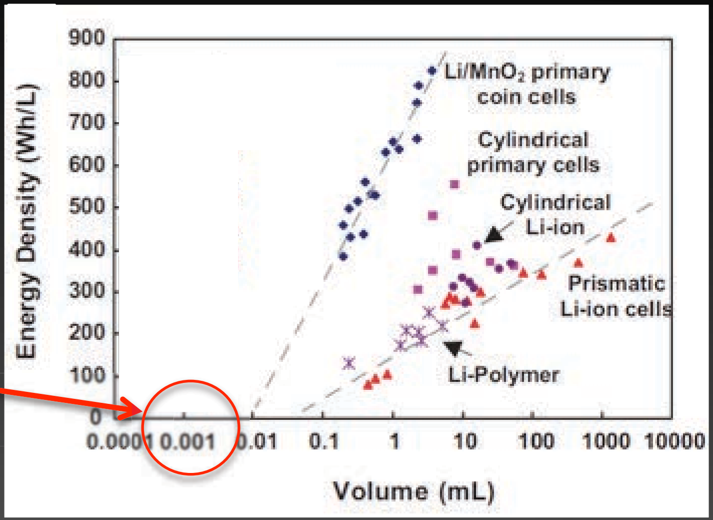
2. *Store energy*
   - micro-batteries w/ high energy and power density

3. Perform function
   - Mechanical
   - Sensing
   - RF

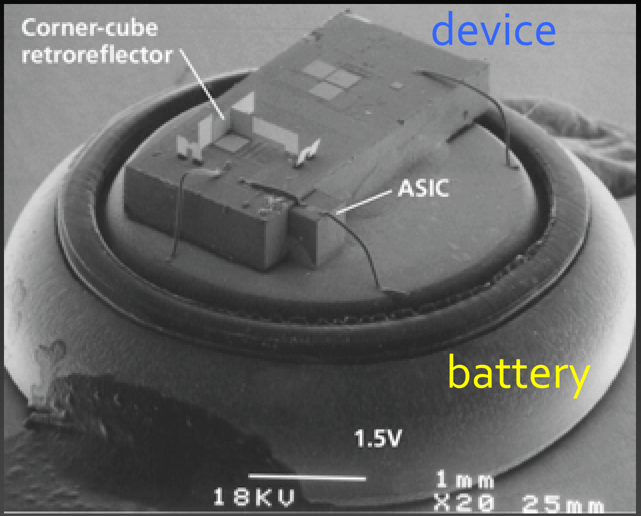


Our goal:
Print 1 mm^3
3D microbatteries

i.e., size of a single grain of sand (!)



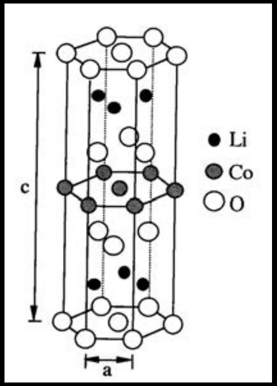
Lai et al., Adv. Mater. 2010



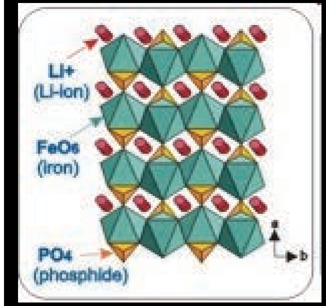
Warneke et al., Computer 2001

Key Factors Influencing Power & Energy Density

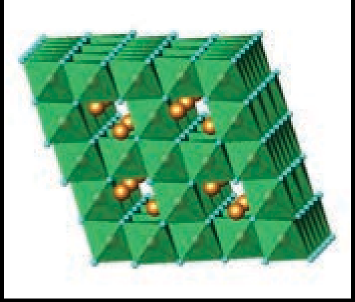
1. Materials Design
   - High output voltage through design of the two half electrode reactions
   - High ion diffusion coefficients (H^+, Li^+ in host materials)
   - New light-weight host materials
   - Fast reaction kinetics



$LiCoO_2$



$LiFePO_4$



$LiMn_2O_4$

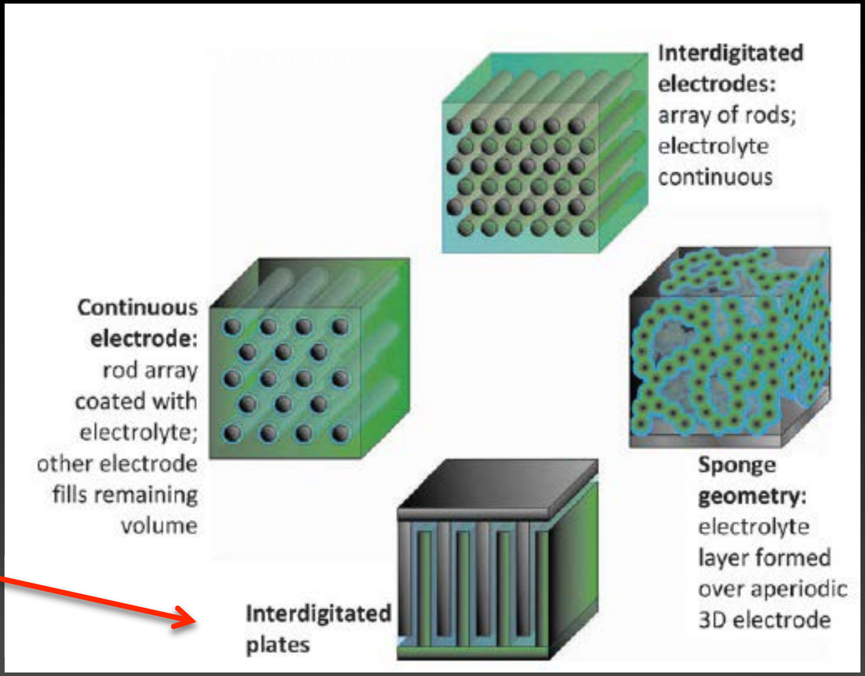
2. Structure Design
   - 3D electrode architecture
   - Large surface area
   - Thin film of active materials

REDUCE TRANSPORT LENGTHS

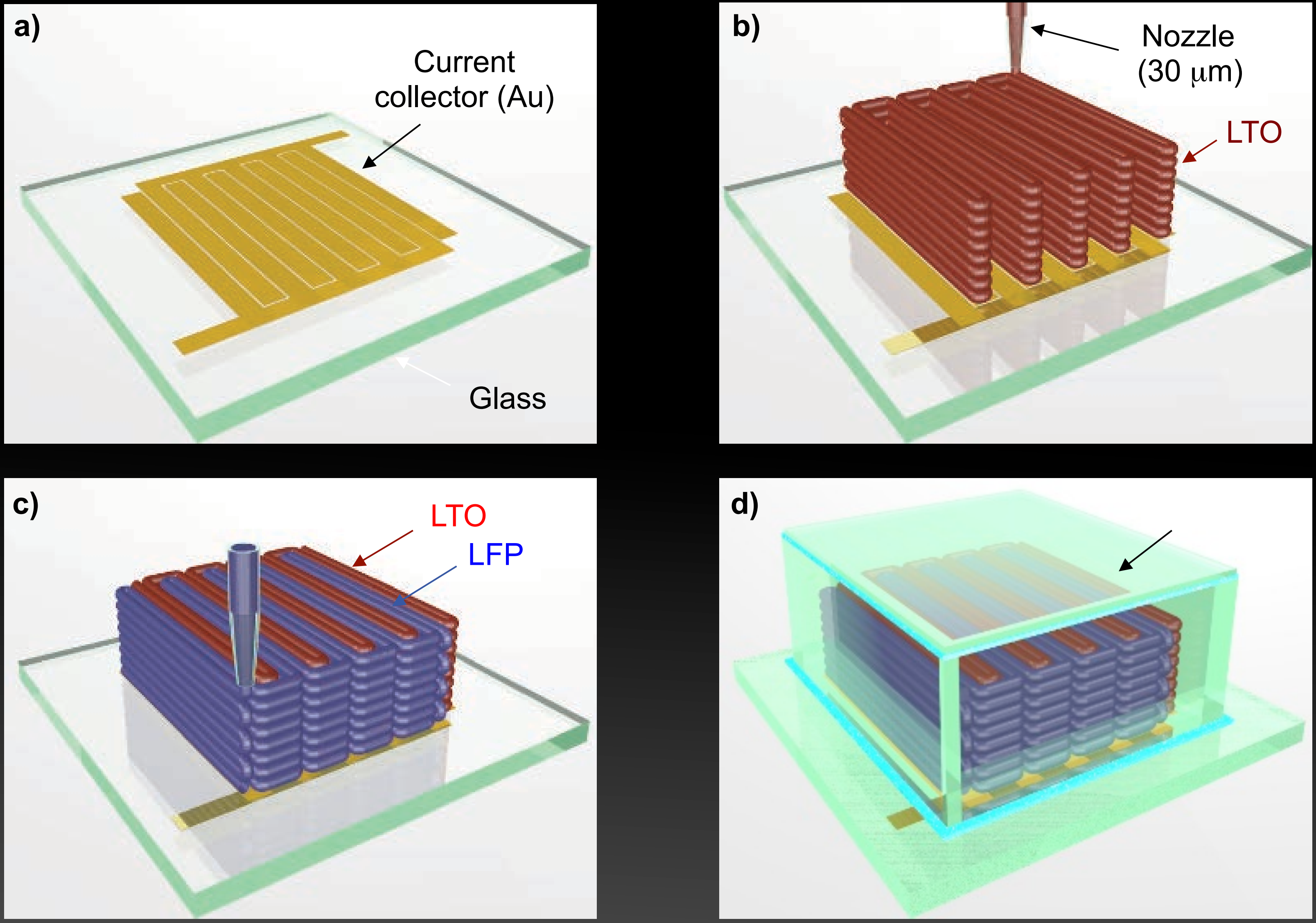
Ahn

Wei

Our Focus:
3D interdigitated microbatteries

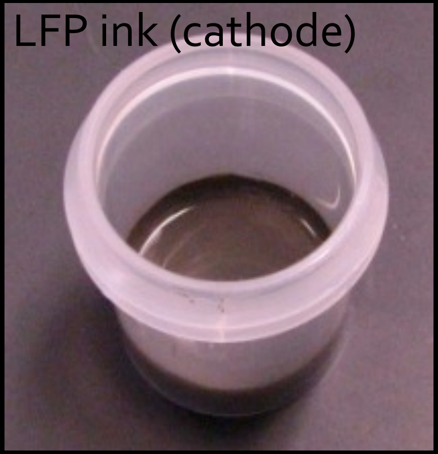


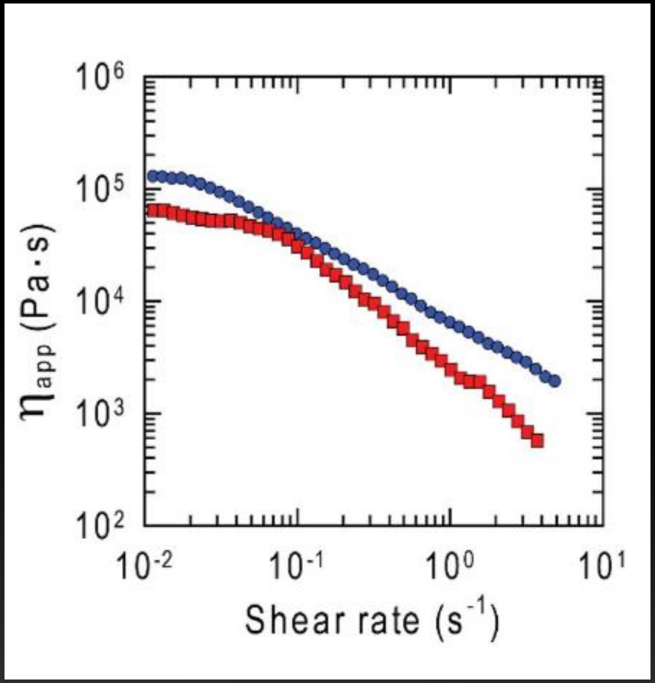
Printing 3D Interdigitated Microbatteries

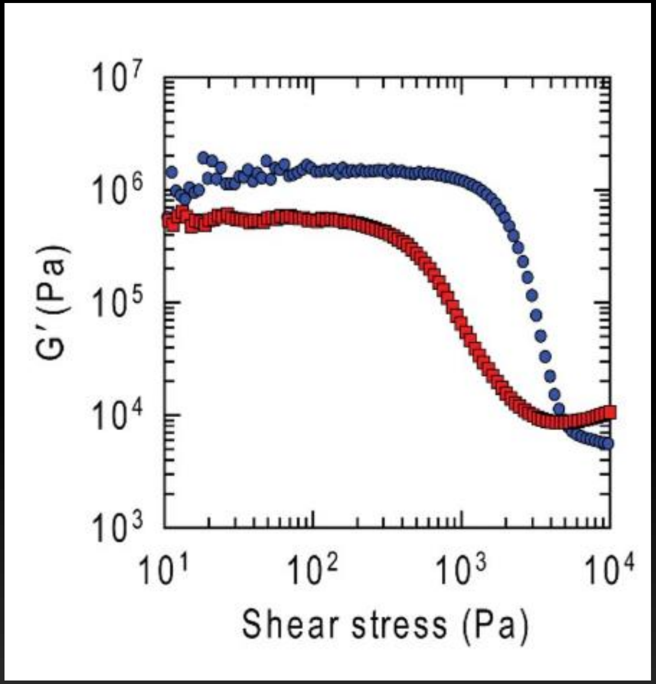


K. Sun, Lewis, Dillon et al, *Adv. Mater.* 2013

Ink Viscosity and Elastic Modulus

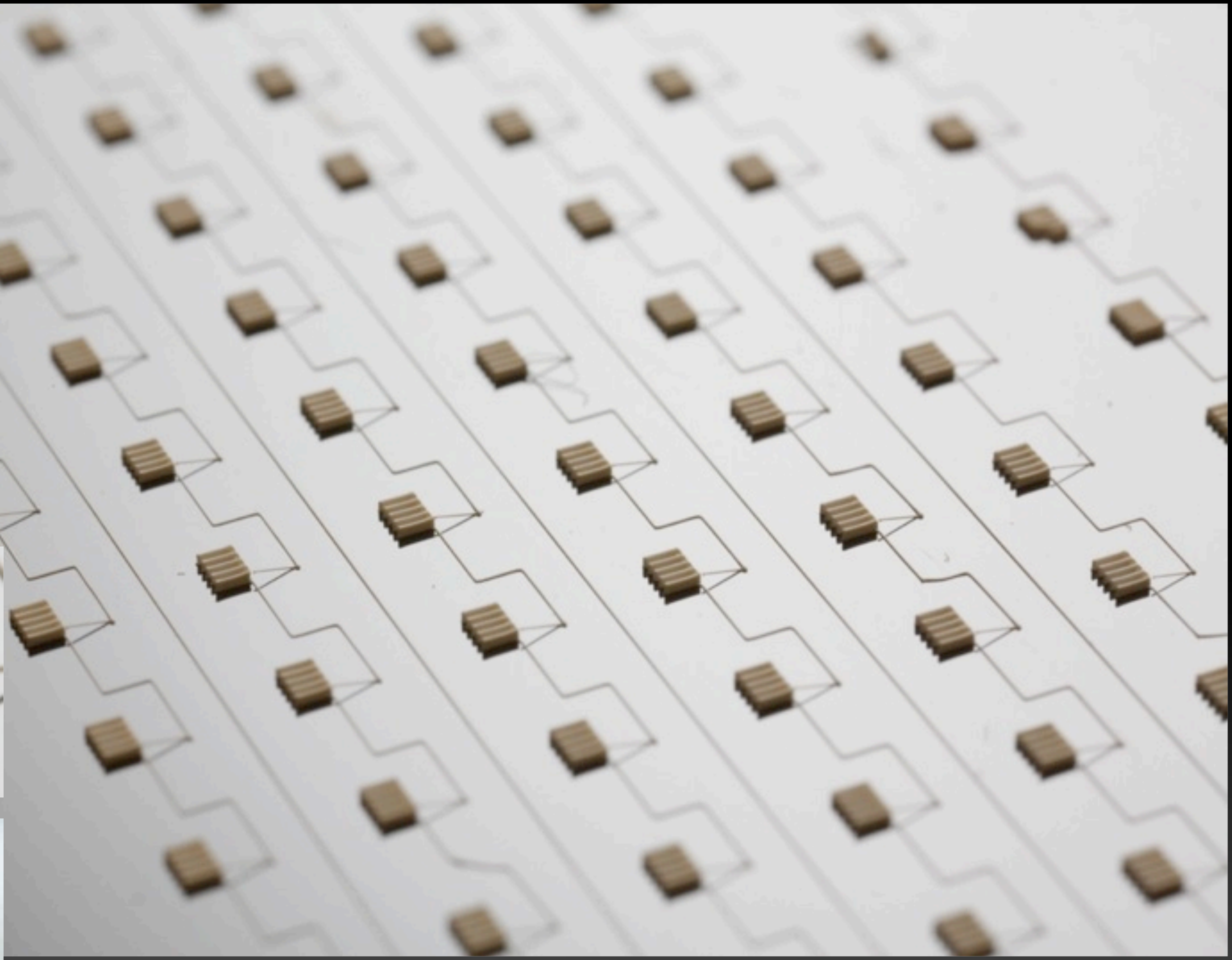


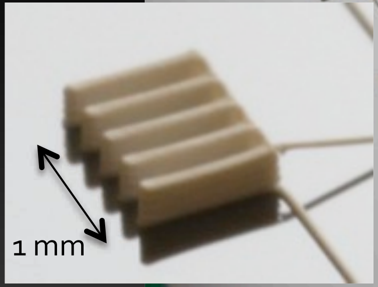




K. Sun, Lewis, Dillon et al, *Adv. Mater.* 2013

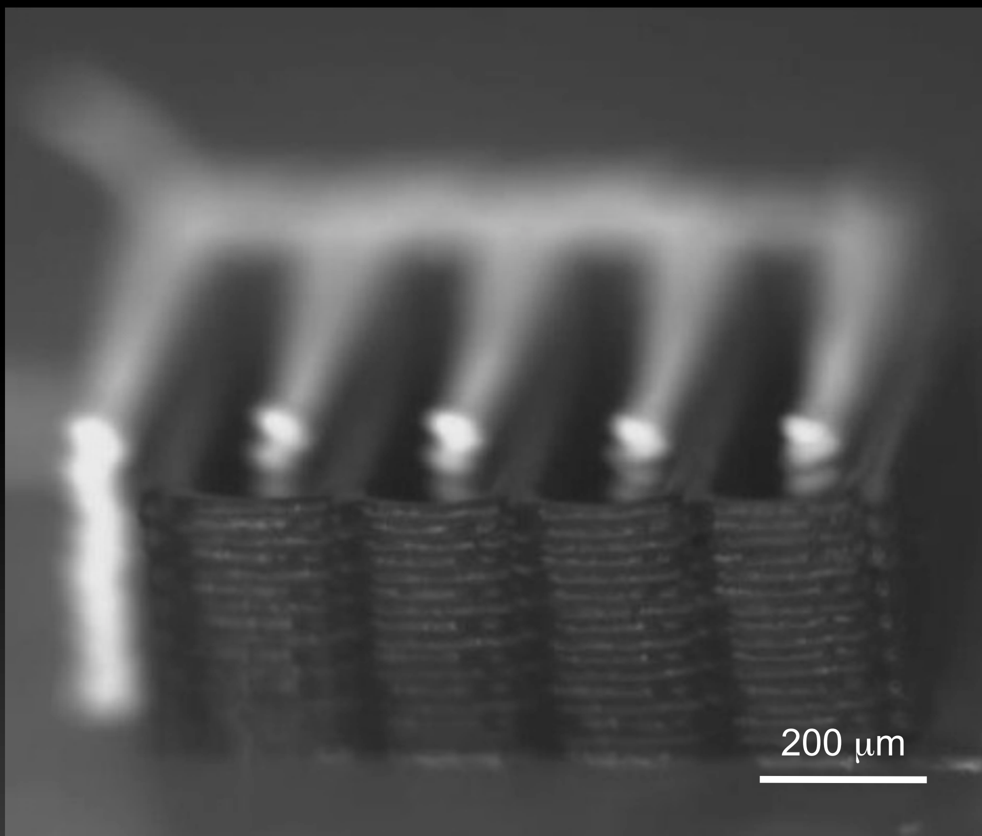
Printing High Aspect Ratio Structures

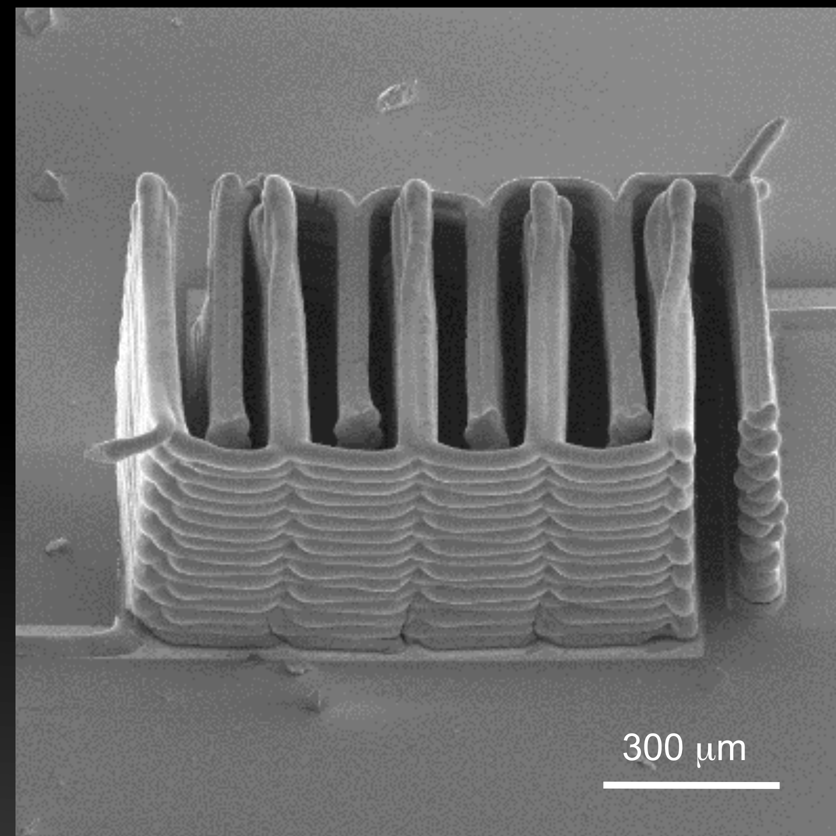




- each microbattery equivalent in size to a single grain of sand

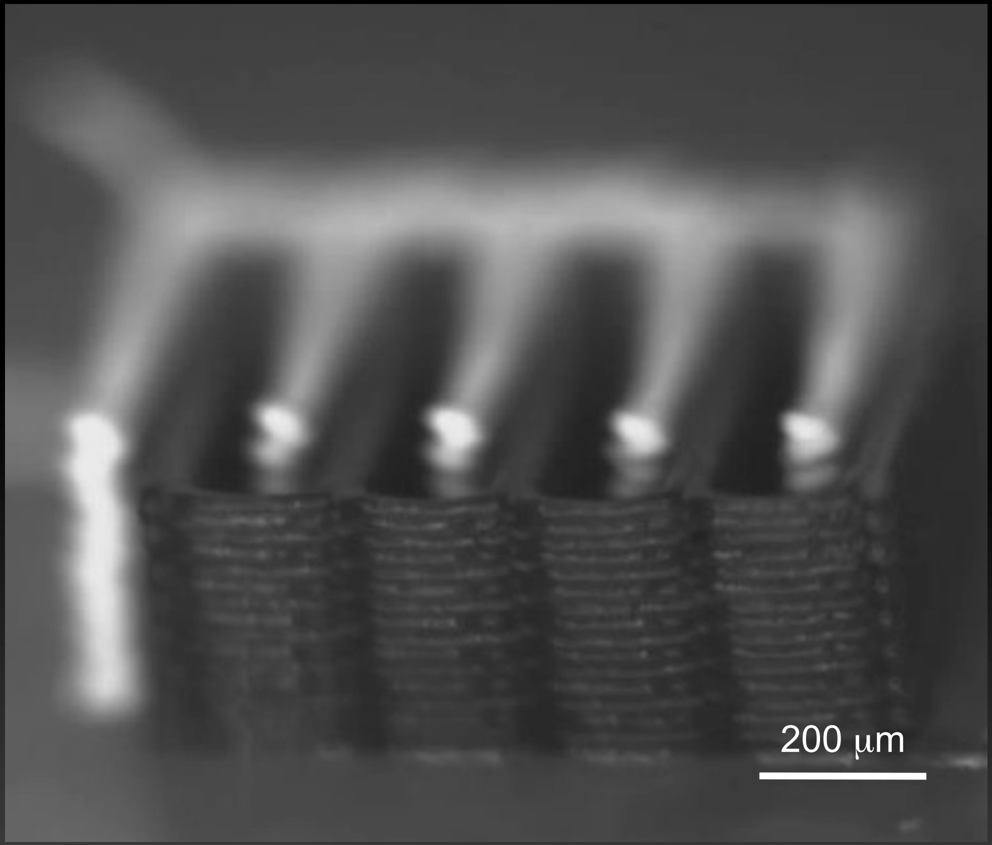
Printed 3D Interdigitated Microbattery

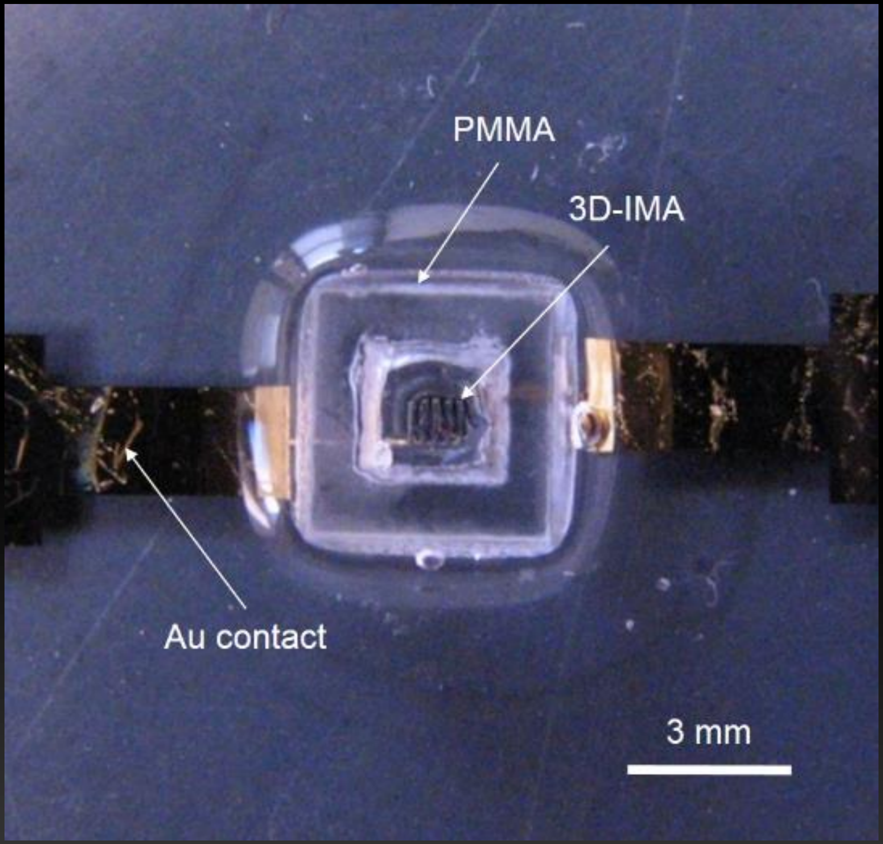




K. Sun, Lewis, Dillon et al, *Adv. Mater.* 2013

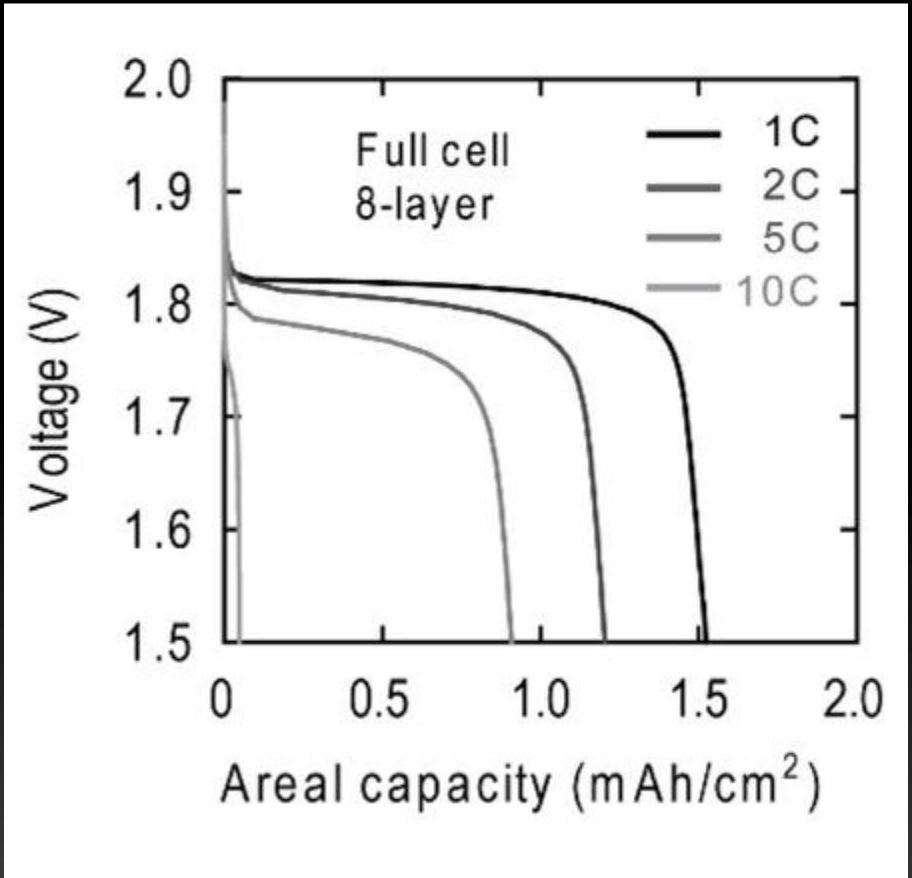
Printed and Packaged 3D Microbattery

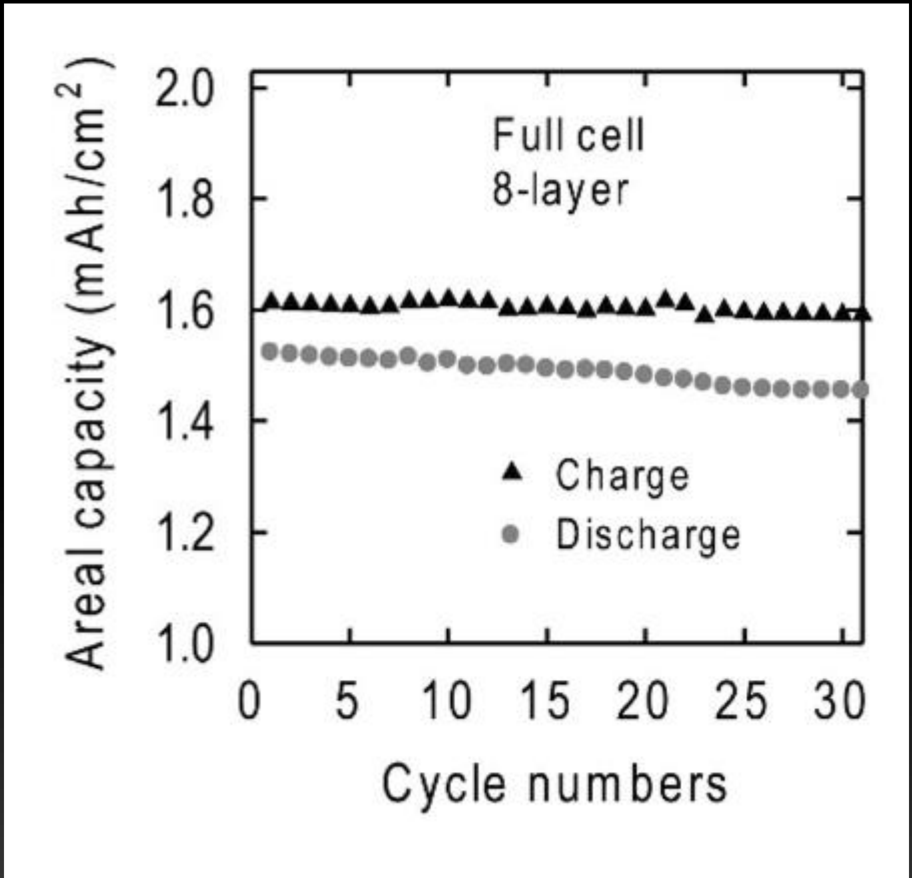




K. Sun, Lewis, Dillon et al, *Adv. Mater.* 2013

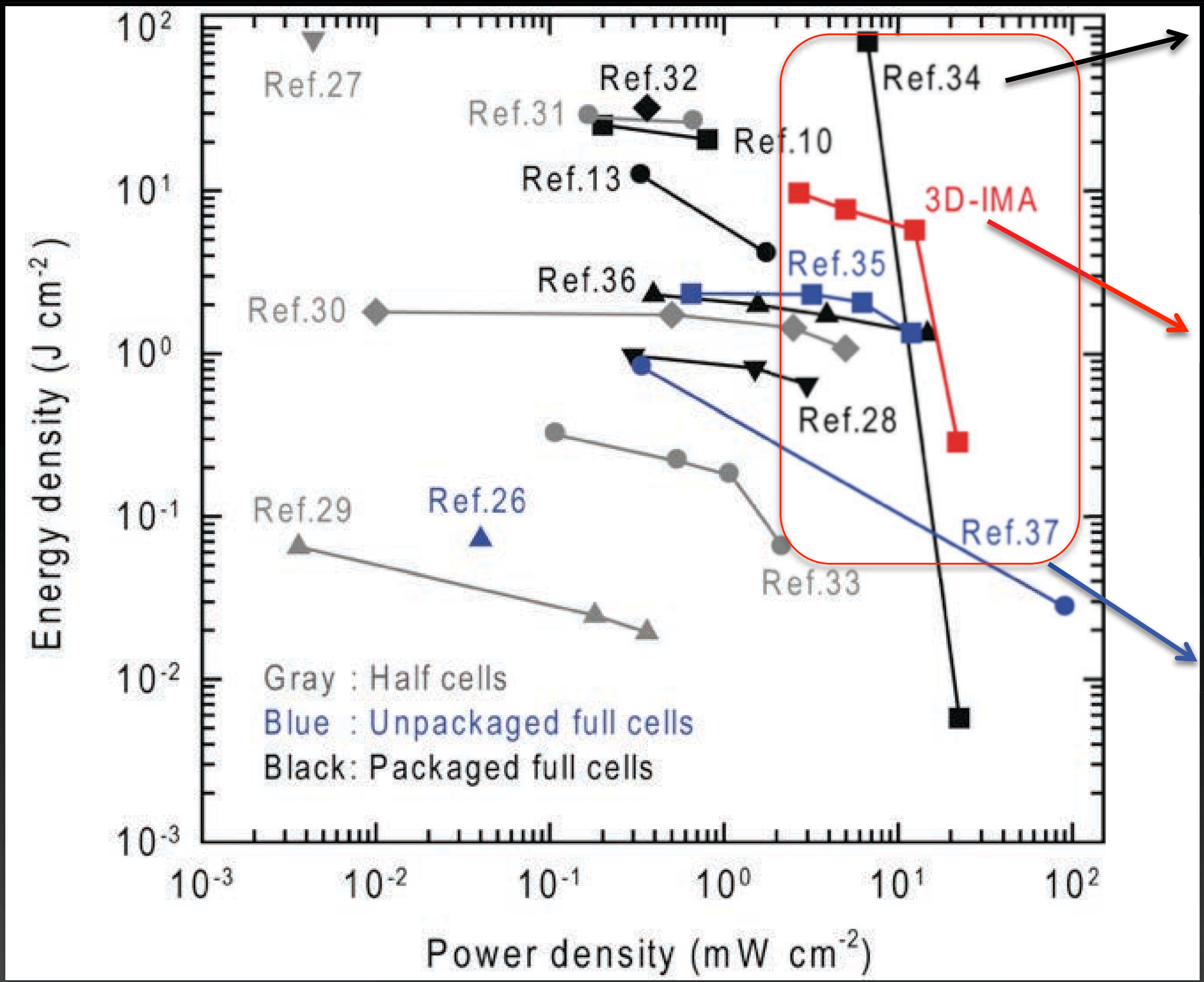
LFP-LTO Full Cell Properties



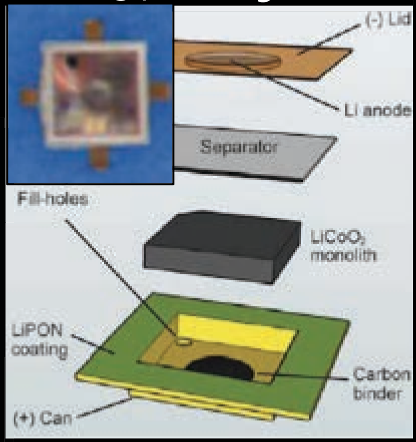


K. Sun, Lewis, Dillon et al, *Adv. Mater.* 2013

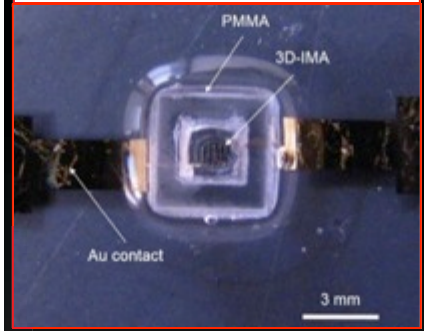
Microbattery Performance



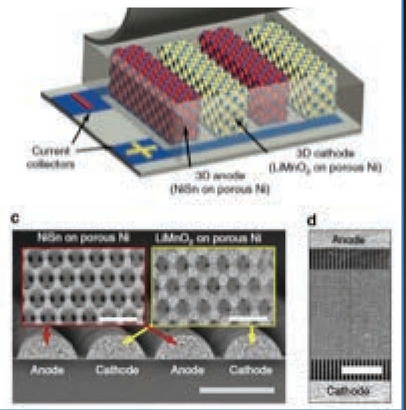
Ref 34: Chiang (MIT)



3D-IMA (Lewis, Dillon)

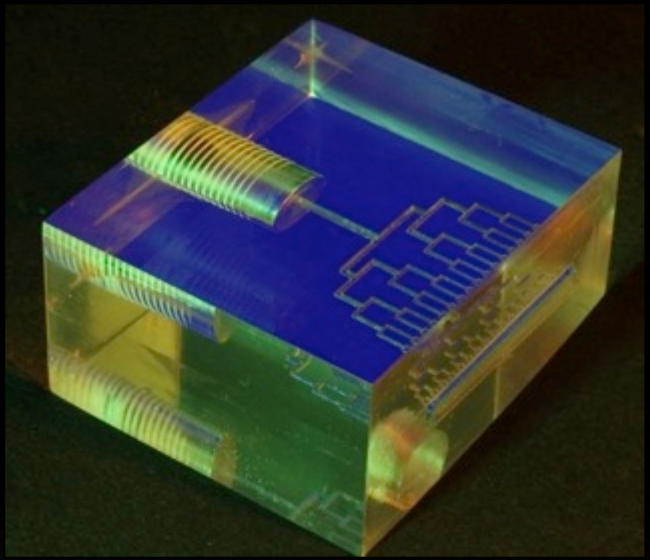


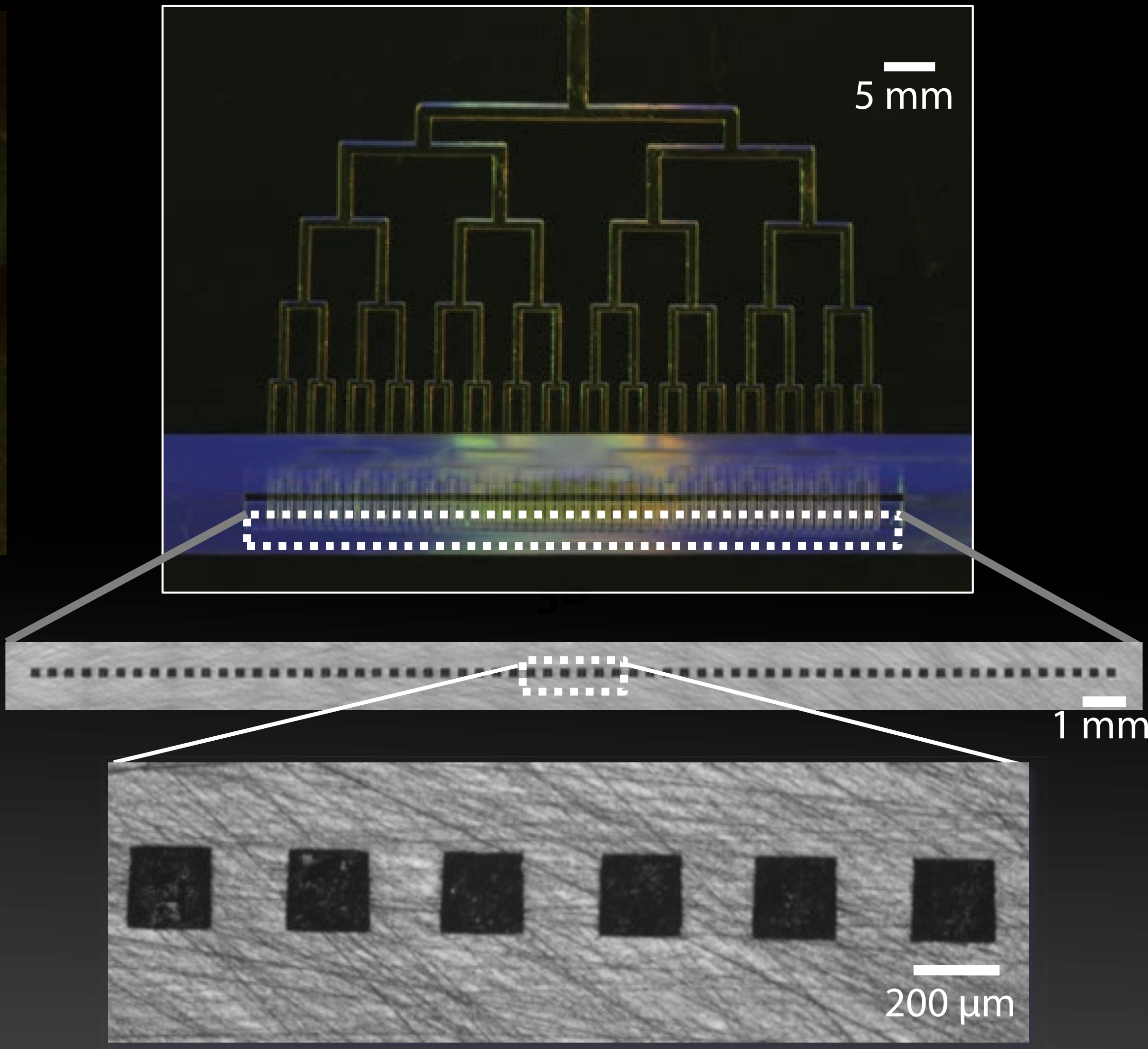
Ref 37: Braun, King (UIUC)



areal densities | 1st gen printed batteries exhibit exceptional performance!

High throughput 3D printing





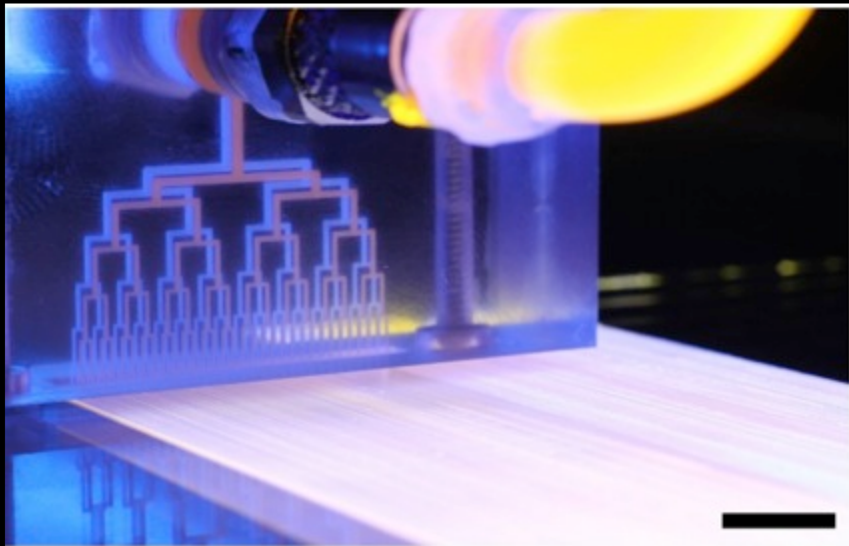
Multinozzle design based on Murray's law:

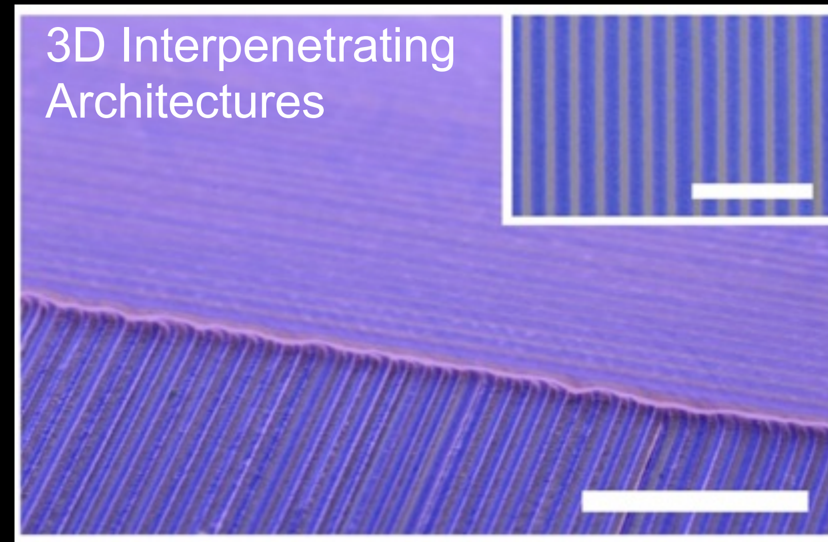
$$r^3_{parent} = \sum r^3_{branch\_generation}$$

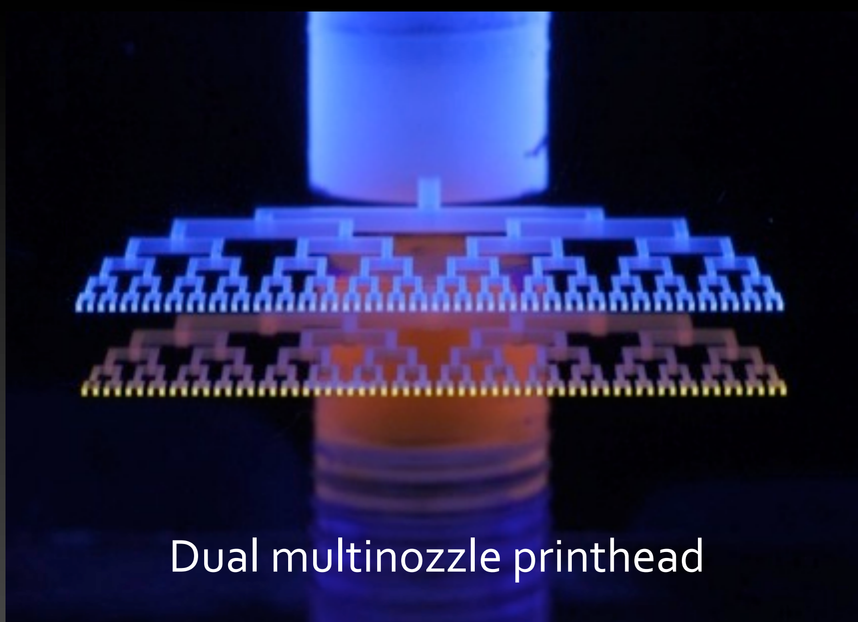
Hierarchical branching network
Created by CNC milling

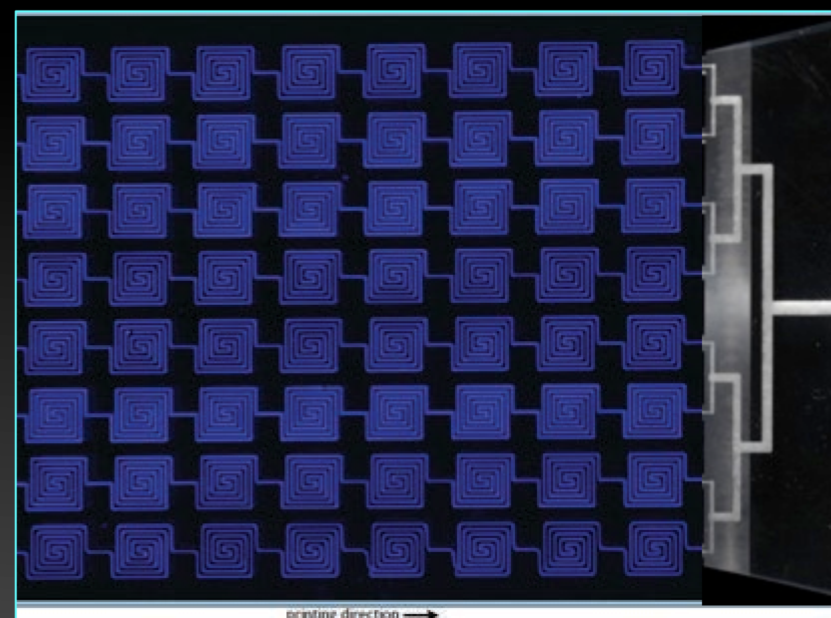
All 64 nozzles are 205±3 µm on a side

High throughput printing of 3D architectures









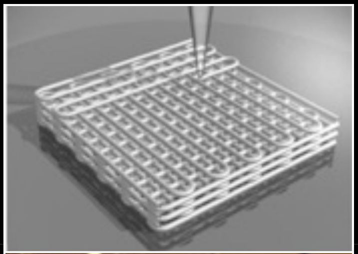
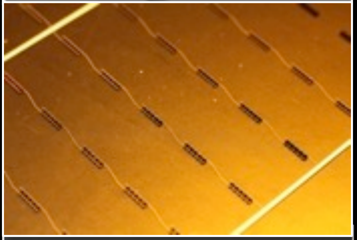
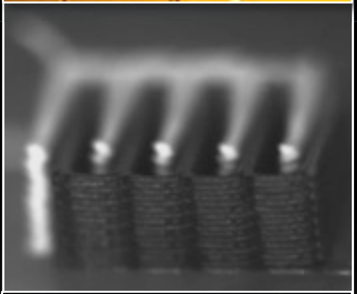
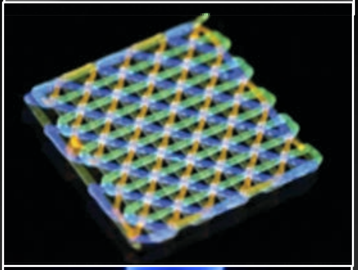
8-nozzle array

Large-area (1 m²) 3D structures printed in minutes using multinozzle printheads

Summary

- Created model and functional inks with controlled flow behavior
- Printed flexible electronics, photovoltaics, and sensors from conductive inks
- Printed 3D Li-ion microbatteries
- Implemented new multimaterial 3D printing
- Designed and implemented microvascular nozzle arrays for high throughput printing

expediting transformation from rapid prototyping
to manufacturing of advanced materials


Thank you!

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