Printing Functional Materials

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3D Printing – Design, Print, Innovate

Broad range of commercial printers and solidification schemes (photocuring, $\Delta T$, 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, $\Delta T$, laser sintering, drying, etc.)

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

(1) Materials flexibility
(2) Ability to pattern fine features ($<100 \, \mu m$)
(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 and 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 cm³ ± 50 nm
V = 0.1 - 10 mm/s

Large Area, High Speed Stage

1m²x10 cm ± 5 µm
V = 1 - 1000 mm/s

High precision, large area, and high speed stages
+ integrating multiple 3D printheads

e.g., FDM
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.

![Ink filament printing](image)

- Continuous filament is extruded through deposition nozzle.
- 30 micron nozzle.

![Viscosity and Moduli](chart)

- Viscosity, \( \eta \) (Pas):
  - Shear thinning
  - Newtonian

- Moduli (Pa):
  - Solid-like
  - Fluid
  - \( G' \)
  - \( G'' \)

- 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

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colloidal inks
fugitive inks
nanoparticle inks
polyelectrolyte inks
sol-gel inks

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250 μm 250 nm

decreasing feature size
Reactive silver inks for integrated electronics

Walker, Lewis JACS (2012); Patent filed
* 90% bulk conductivity at 100°C
Silver particle inks for integrated electronics

Starting Materials

- Silver source: AgNO₃
- Stabilizer: Poly(acrylic acid), PAA
- Reductant: Diethanolamine, DEA
- Solvent: Deionized H₂O

Particle Growth

Sonication (60 °C, ~2 h)

Phase Separation

Centrifugation

Homogenization

Add Humectant

20 nm average, 5 – 50 nm distribution

Silver particles inks for printed electronics

Silver inks are highly conductive as-printed

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

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

Printing interconnects and bus bars

Sparse array of PV cells; finer interconnects

Bus bars
Interconnects
InP cells

10 cm x 10 cm

610 µm nozzle
Bus bars

30 µm nozzle
Interconnects

In collaboration with Semprius and SAIC
Flexible concentrator photovoltaics

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).

Efficiency ~71%

Resonant at ~1.7 GHz

Embedded Electronics
(carbon ink printed in polymer matrix)

400 μm nozzle

As printed

After encapsulation

200 μm nozzle

0% stretch

300% stretch

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 mm³ 3D microbatteries
i.e., size of a single grain of sand (!)
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

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

REduce TRANSPORT LENGTHS

Our Focus:
3D interdigitated microbatteries
Printing 3D Interdigitated Microbatteries

Ink Viscosity and Elastic Modulus

LFP ink (cathode)

LTO ink (anode)

Printing High Aspect Ratio Structures

- each microbattery equivalent in size to a single grain of sand
Printed 3D Interdigitated Microbattery

Printed and Packaged 3D Microbattery

LFP-LTO Full Cell Properties

Microbattery Performance

areal densities | 1st gen printed batteries exhibit exceptional performance!
High throughput 3D printing

Multinozzle design based on Murray’s law:

\[ r_{\text{parent}}^3 = \sum r_{\text{branch \_ generation}}^3 \]

Hierarchical branching network
Created by CNC milling

All 64 nozzles are 205±3 \( \mu \text{m} \) on a side
High throughput printing of 3D architectures

Dual multinozzle printhead

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