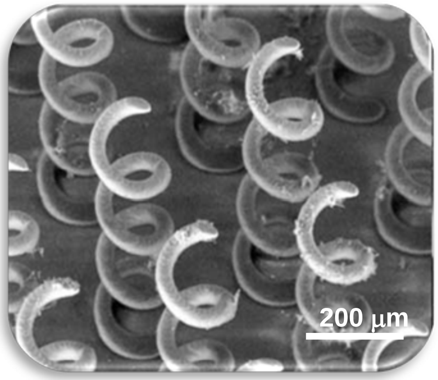
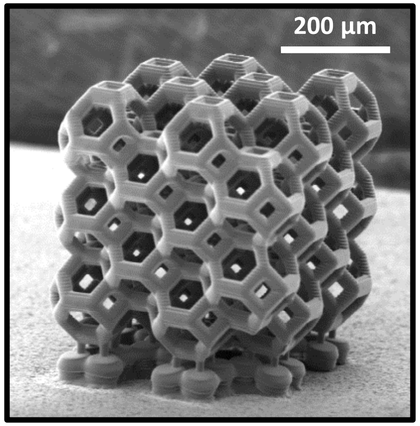
# Advanced Manufacturing To Enable New Solvents and Processes For Carbon Capture

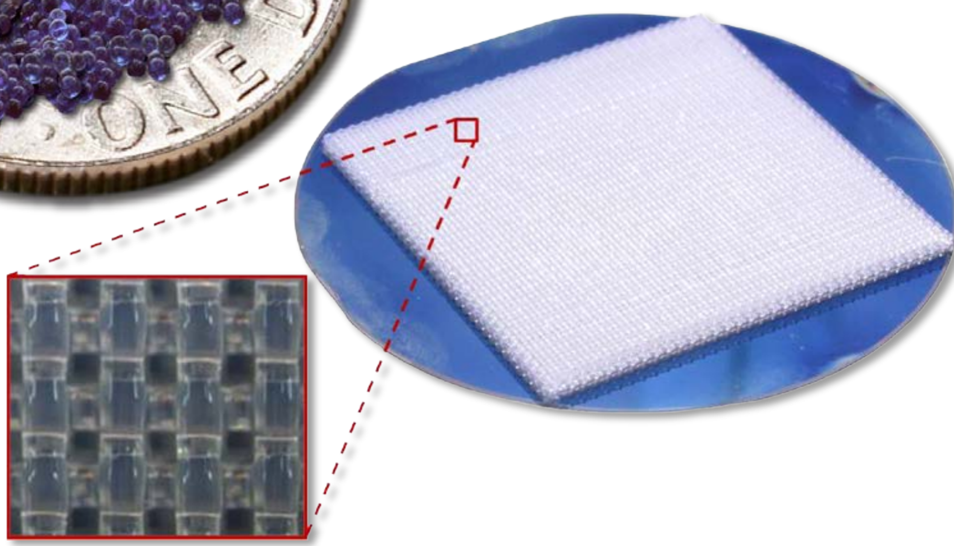
June 25, 2015

NETL $CO_2$ Capture Technology Meeting

Joshuah K. Stolaroff



Lawrence Livermore National Laboratory

Carnegie Mellon University

HARVARD UNIVERSITY

LLNL-PRES-555917

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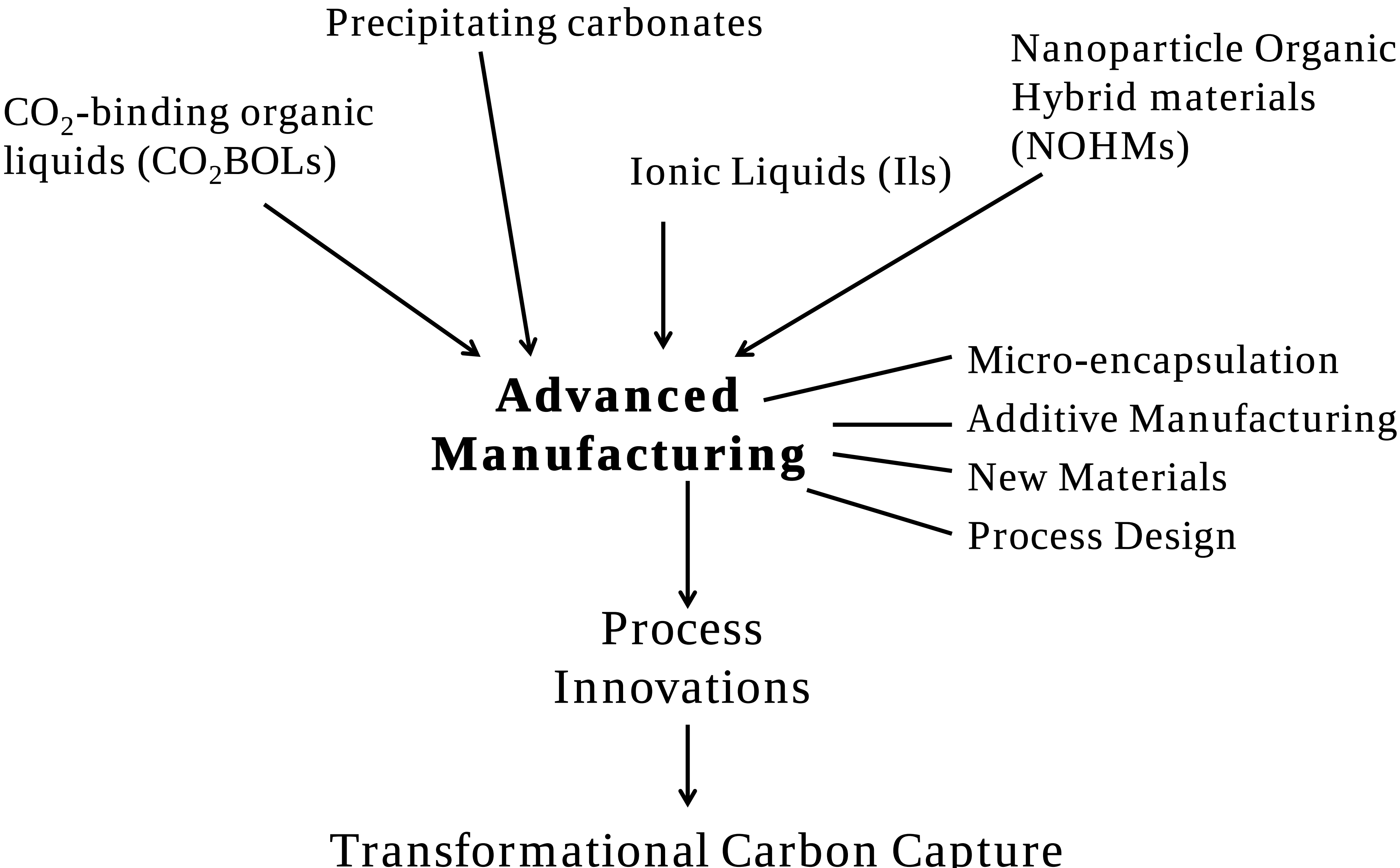
# New fabrication techniques can enable new materials and processes to achieve low-cost carbon capture.



# FEW0194: Advanced Manufacturing To Enable Enhanced Processes And New Solvents For Carbon Capture

## $4.15M over 3 years (April 15, 2015 – April 14, 2018)

Tasks

Encapsulation of Advanced Solvents
$475k/yr

Process design and scaleup with microcapsules
$475k/yr

$CO_2$ absorber design with advanced manufacturing
$250k/yr

Rapid determination of solvent properties via microfluidic reactors
$133k/yr

**Objective:** enable solvent-based transformational carbon capture using advanced manufacturing techniques.

Task Objectives

Demonstrate encapsulation of new solvents with desirable properties for transformational carbon capture.

Identify and refine a suitable process configuration for Microencapsulated $CO_2$ sorbents (MECS).

Identify improvements to absorbers enabled by advanced manufacturing.

Determine properties of candidate solvents via microfluidic techniques.

# Project Team

Lawrence Livermore National Laboratory

Joshuah K. Stolaroff, John J. Vericella, Sarah E. Baker, Eric B. Duoss, Cheng Zhu, William L. Smith, James S. Oakdale, Bill Bourcier, Christopher M. Spadaccini, and Roger D. Aines

Carnegie Mellon University

John Kitchen

Harvard University

David Weitz

# Collaborators

Pacific Northwest National Laboratory

David Heldebrant

Columbia University in the City of New York

Alissa Park

University of Notre Dame

Joan Brennecke

Advanced solvents have some common advantages:

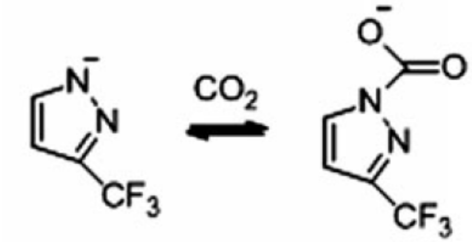
- Lower energy of regeneration
- Low volatility
- Tunability for innovative processes

...and common problems:

- High viscosity
- Water intolerance
- Phase changes
- Slow heat transfer or mass transfer
- High solvent cost

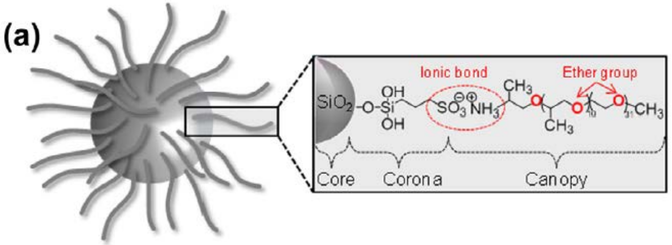
# Some solvents with potential for 30—50% energy savings and specific challenges:

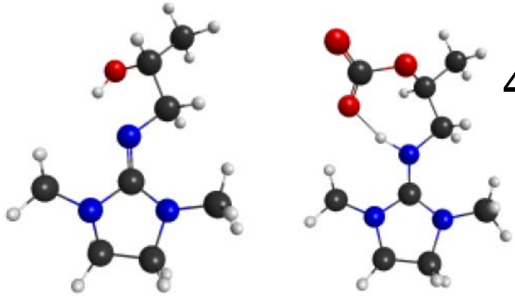

1. **Sodium carbonate** solution: slow $CO_2$ absorption, precipitates solids.




2. **Ionic Liquids**: water intolerance, precipitate solids (PCIL's).

3. **NOHMs**: high viscosity, slow $CO_2$ absorption.



4. **$CO_2$BOLs**: poor heat transfer rates (high viscosity).

→How can advanced manufacturing help?

# Advanced Manufacturing:

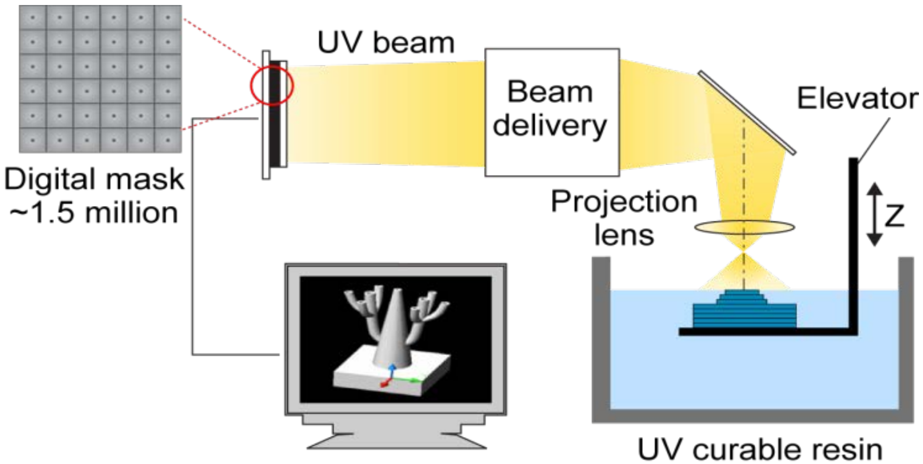
a suite of fabrication techniques characterized by:

- additively assembled parts
- micro- or nano-scale control over structures (micro-architecture)
- micro- or nano-scale assembly of multiple components
- computational or analytical design directly input to the fabrication technique

# Some additive manufacturing techniques under development at LLNL

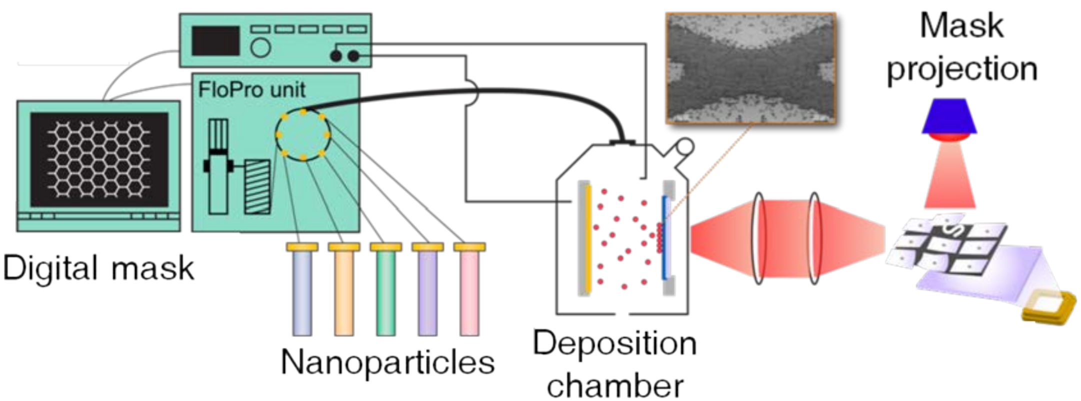
## Projection Microstereolithography (PμSL)

A photochemical and optical technique



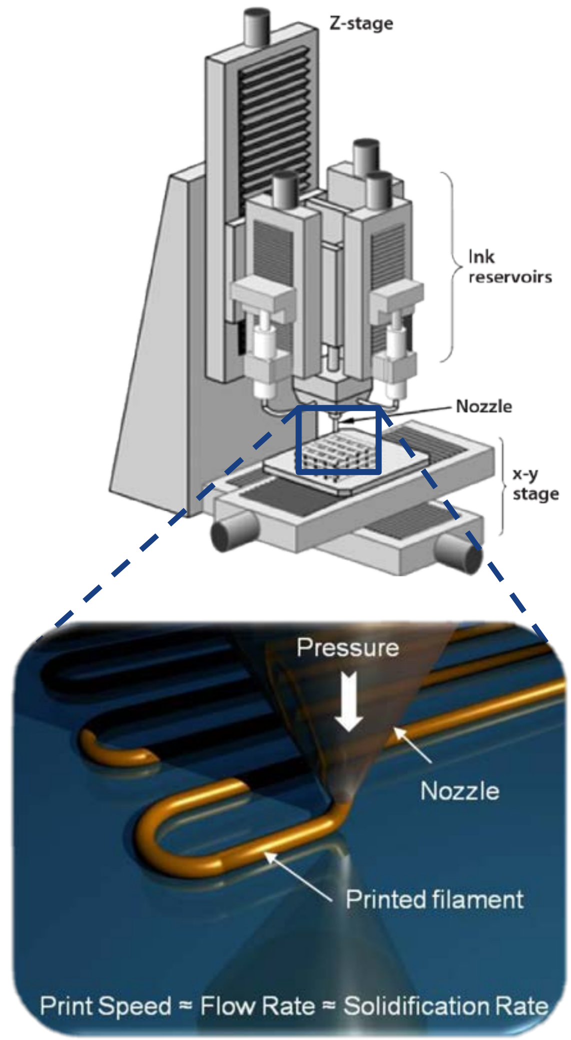

## Electrophoretic Deposition (EPD)

Electric fields transport nanoparticles




## Direct Ink Writing (DIW)

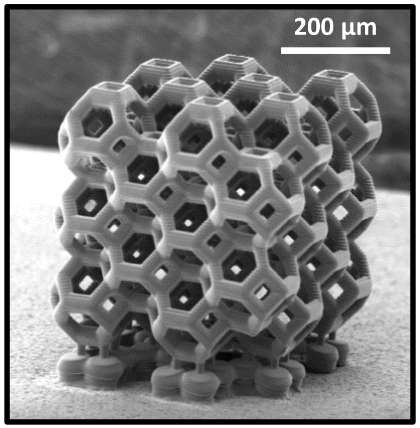
Utilizes unique flow and gelling properties

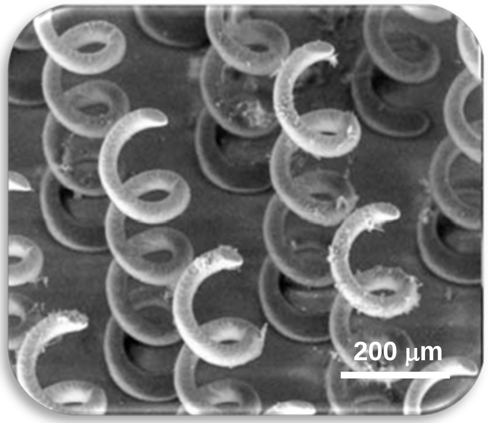


# Some additive manufacturing techniques under development at LLNL

**Projection Microstereolithography (PμSL)**

A photochemical and optical technique

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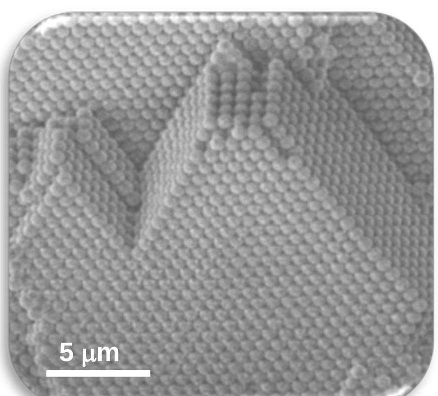
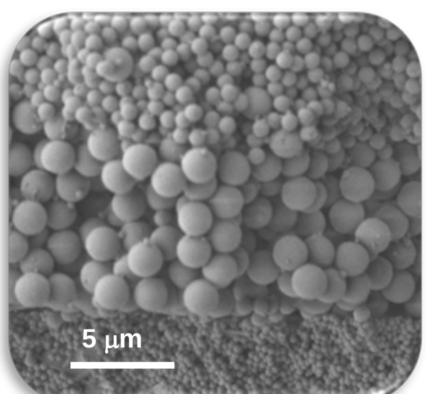
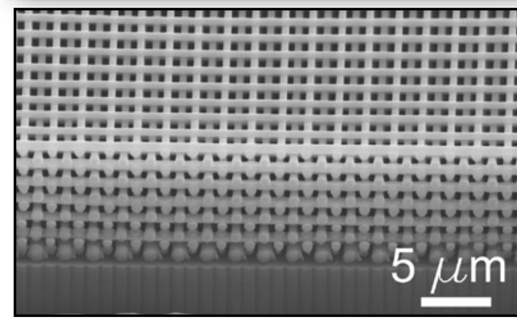
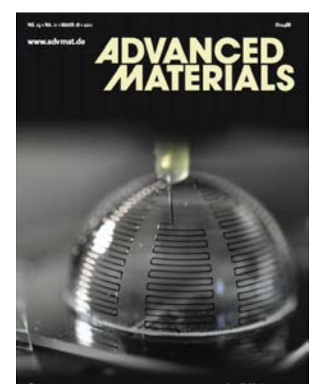



**Direct Ink Writing (DIW)**

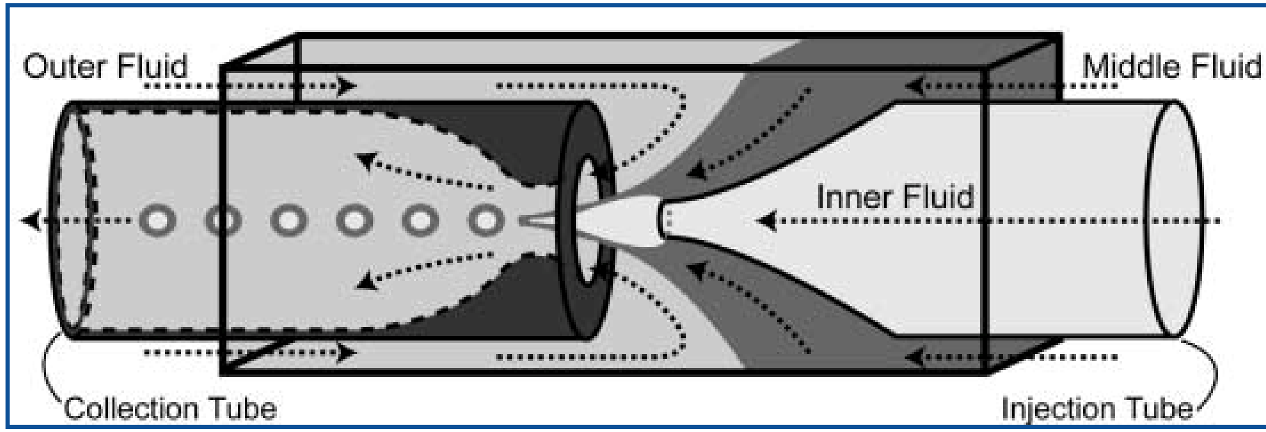
Utilizes flow and gelling properties

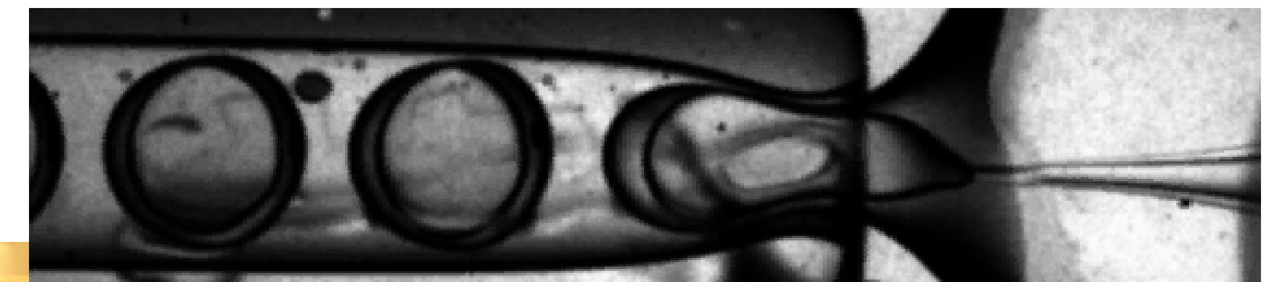


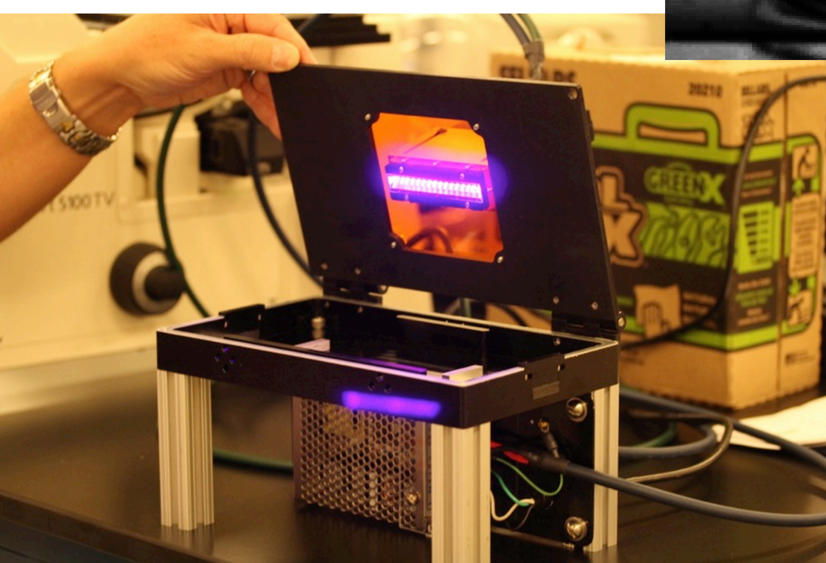



# Microencapsulation: double emulsions are produced in a microfluidic device…

- Control of capsule diameter and shell thickness.
- Encapsulates ~100% of inner fluid
- Core fluid can also have solids
- Production rate: 1-100 Hz



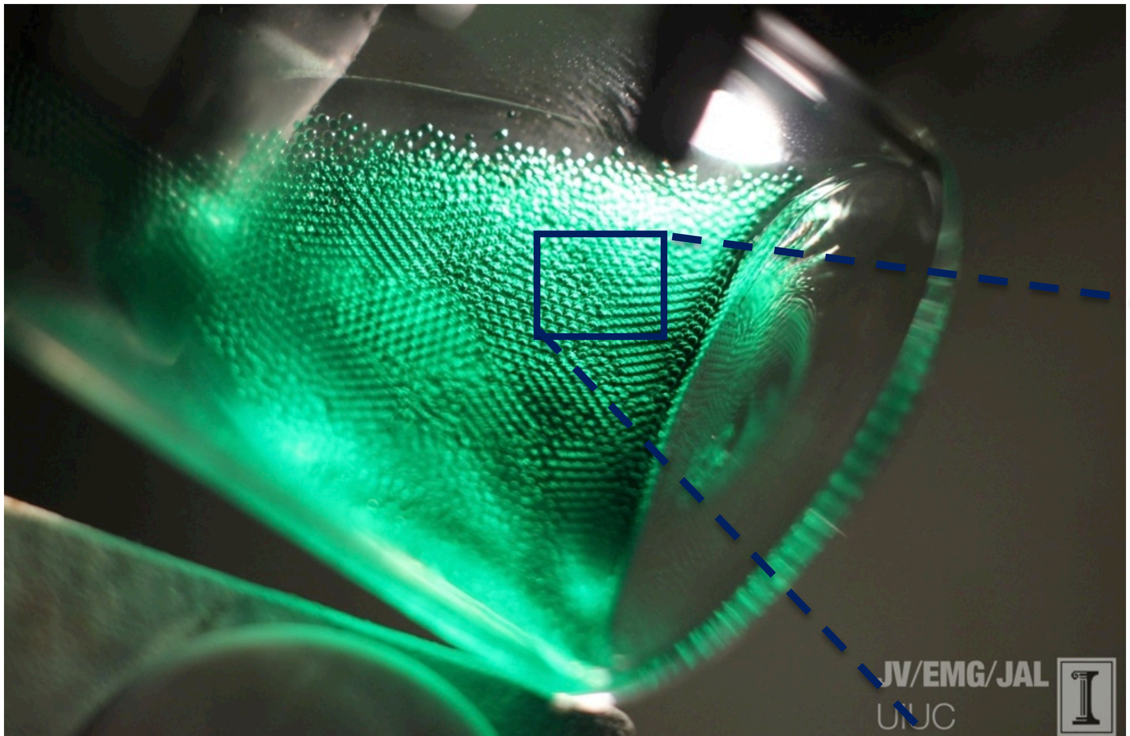





…and then cured with UV light.

Micro-encapsulated Carbon Sorbents (MECS):

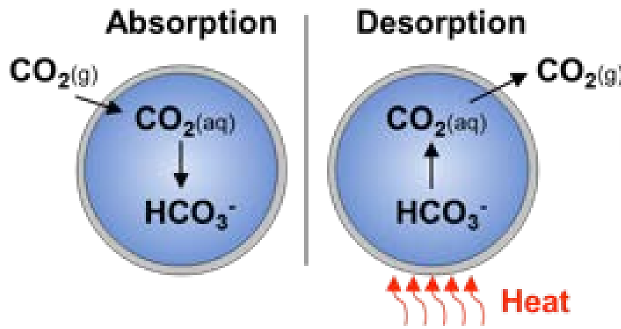
Liquid solvents or slurries encased in thin, permeable polymer shells

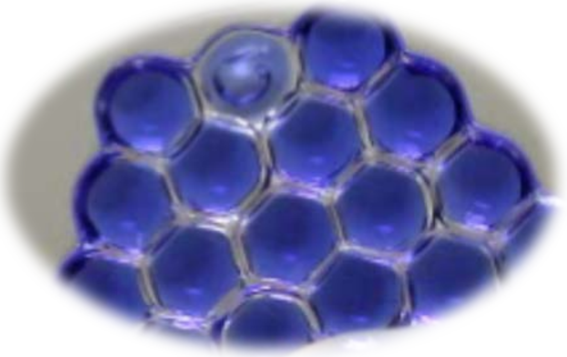



- Multiple solvents, shell materials, and sizes produced

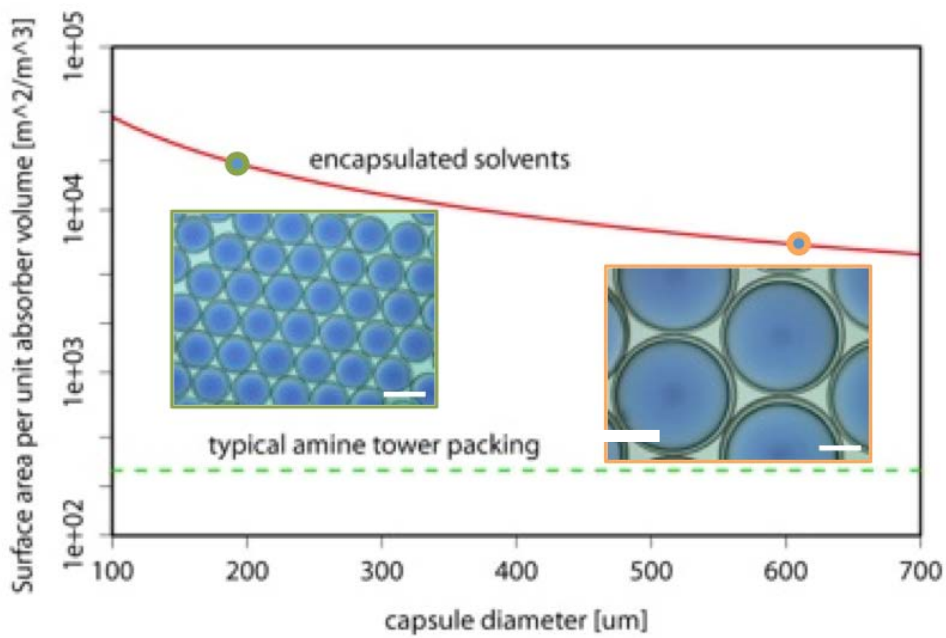
# Microencapsulation enhances kinetics.

$CO_2$ absorbs through shell

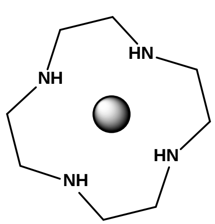


Surface area formed by capsule, not a tower



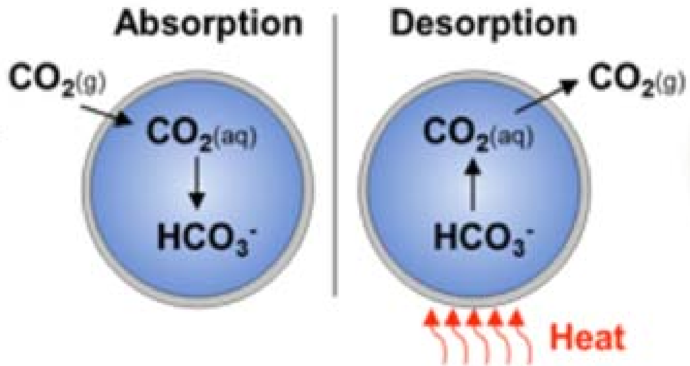

Embedded catalyst further enhances kinetics



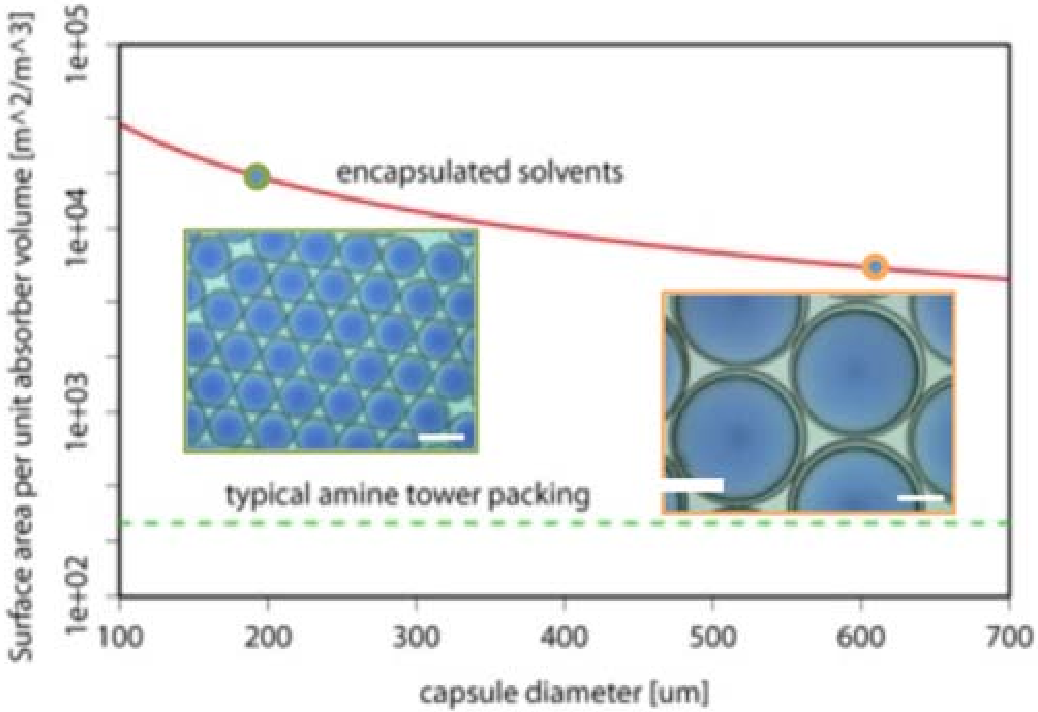

"Zn-Cyclen"

# Microencapsulation enhances kinetics.

$CO_2$ absorbs through shell




Surface area formed by capsule, not a tower

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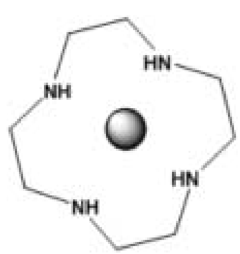
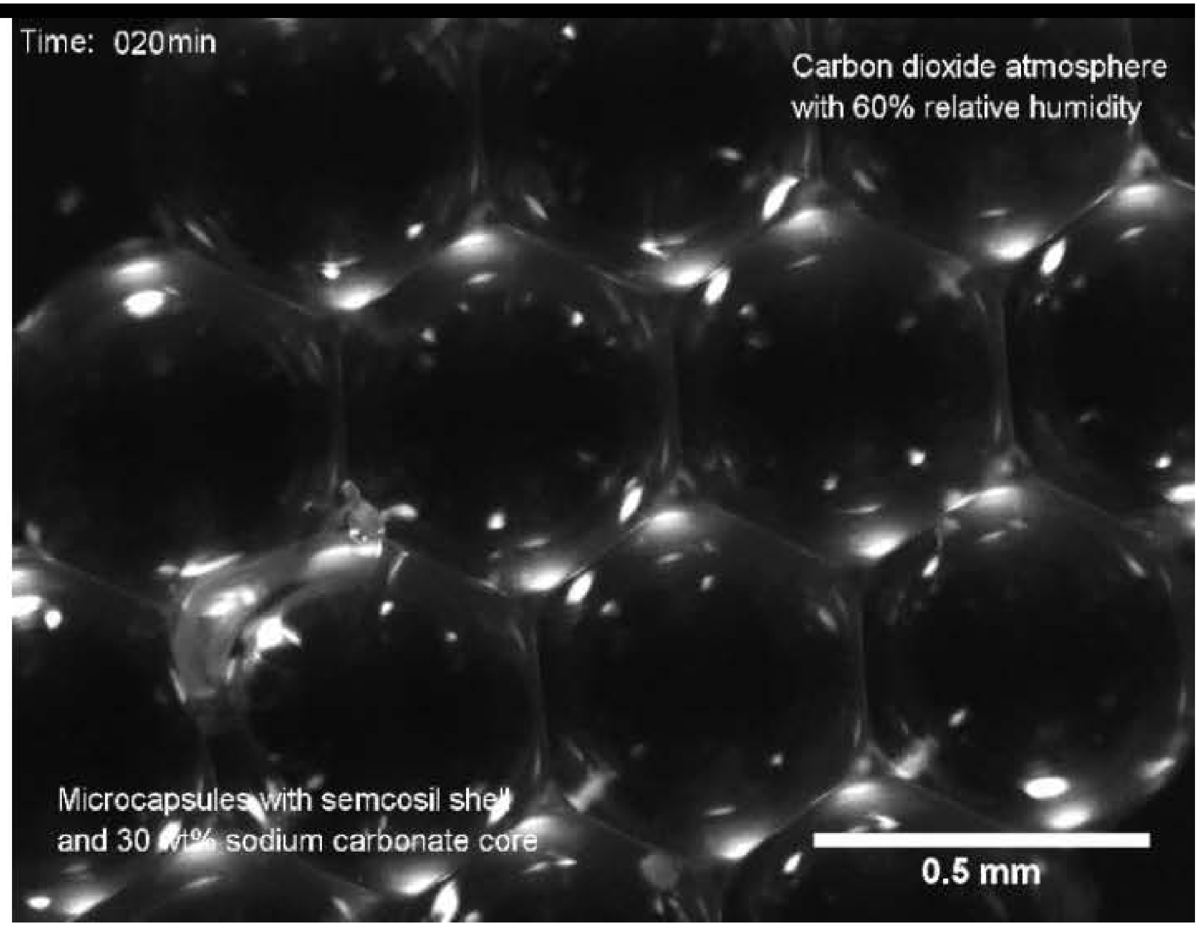



"Zn-Cyclen"

# Microencapsulation enables mixed phases and viscous solvents.

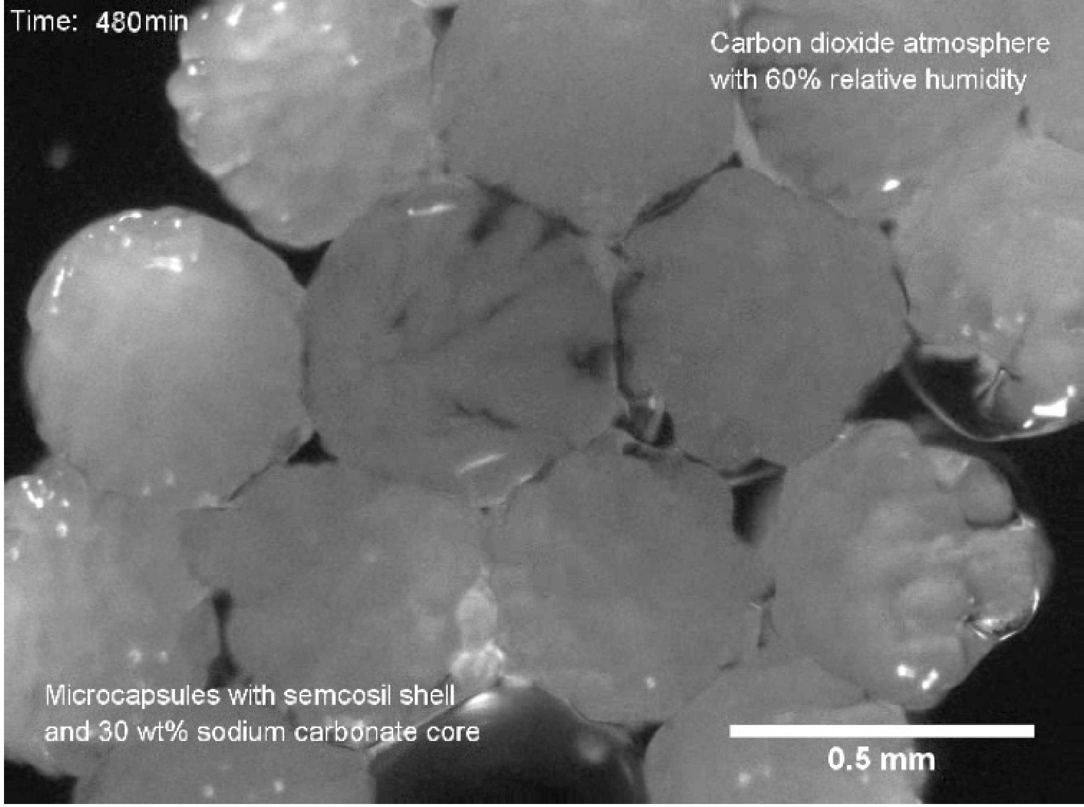
30 wt% $Na_2CO_3$ capsules exposed to $CO_2$ precipitating Nacholite→




Encapsulating slurry of glass bubbles↓

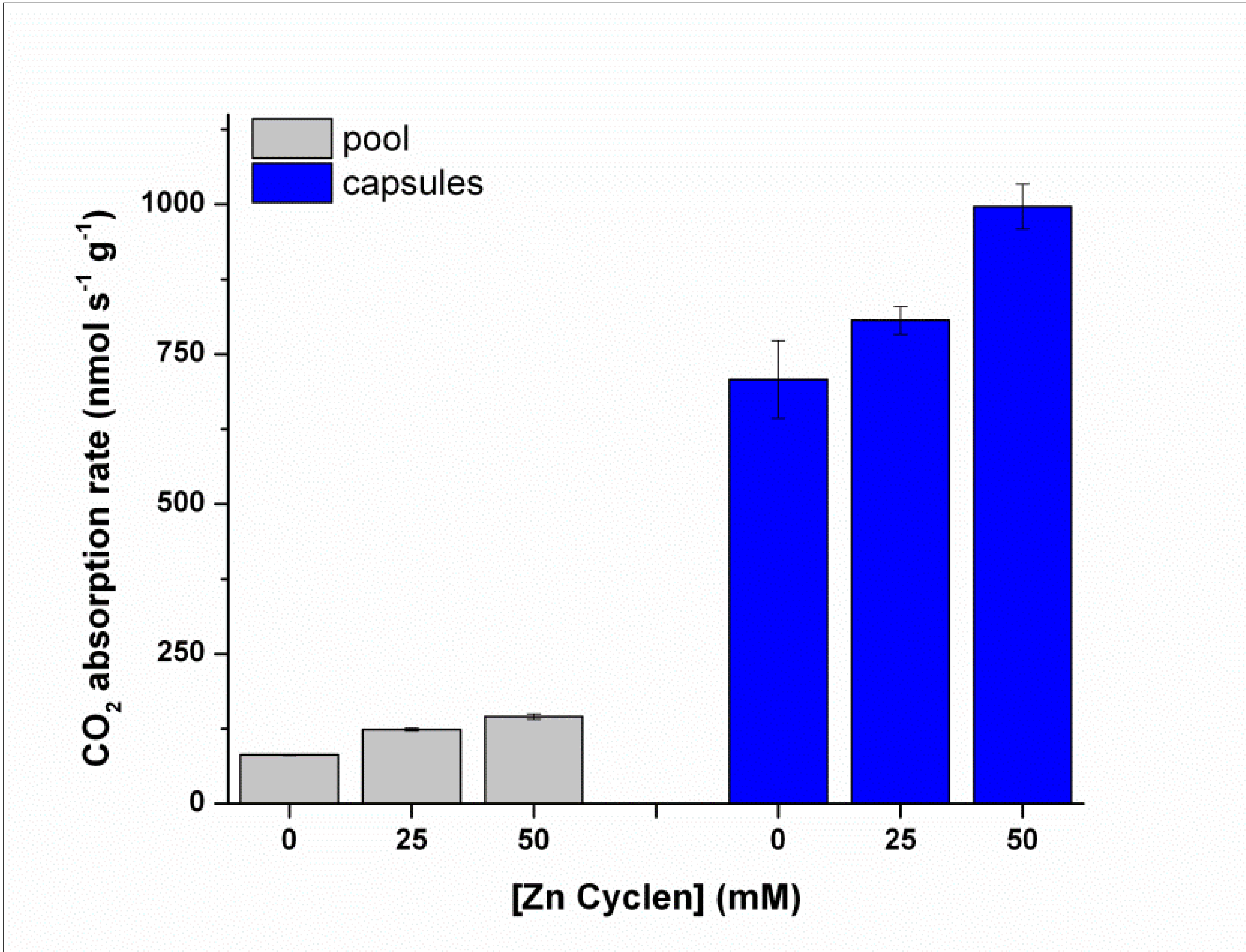
# Microencapsulation enables mixed phases and viscous solvents.

30 wt% $Na_2CO_3$ capsules exposed to $CO_2$ precipitating Nacholite➞




Encapsulating slurry of glass bubbles⬇

# Encapsulation increases capture rate of carbonates by 10x compared to same volume of liquid.



Process options same as for solids:

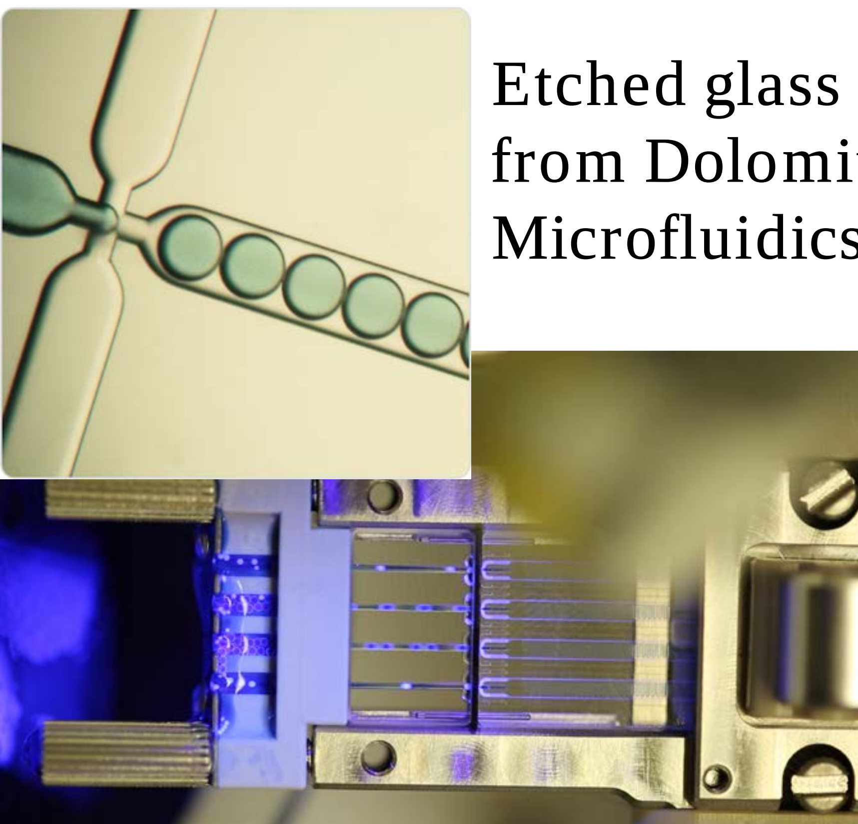
- Fluidized bed
- Moving Bed
- Fixed bed

Thermally regenerable for many cycles (80 tested).

# Challenges and planned work

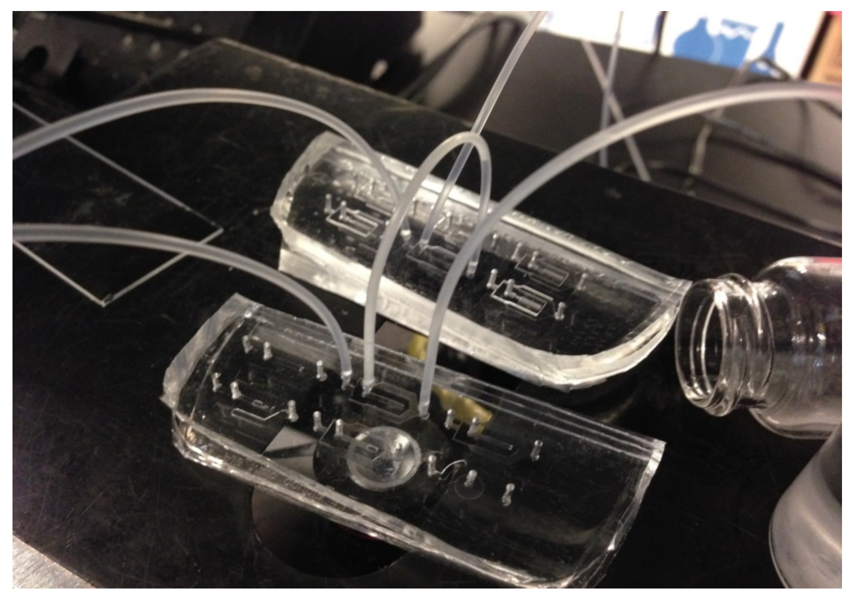
# Challenge: Capsule Production Scale-up

- Bulk emulsion methods exist, but yield a distribution of capsule properties.
- Two microfluidic production methods being pursued.

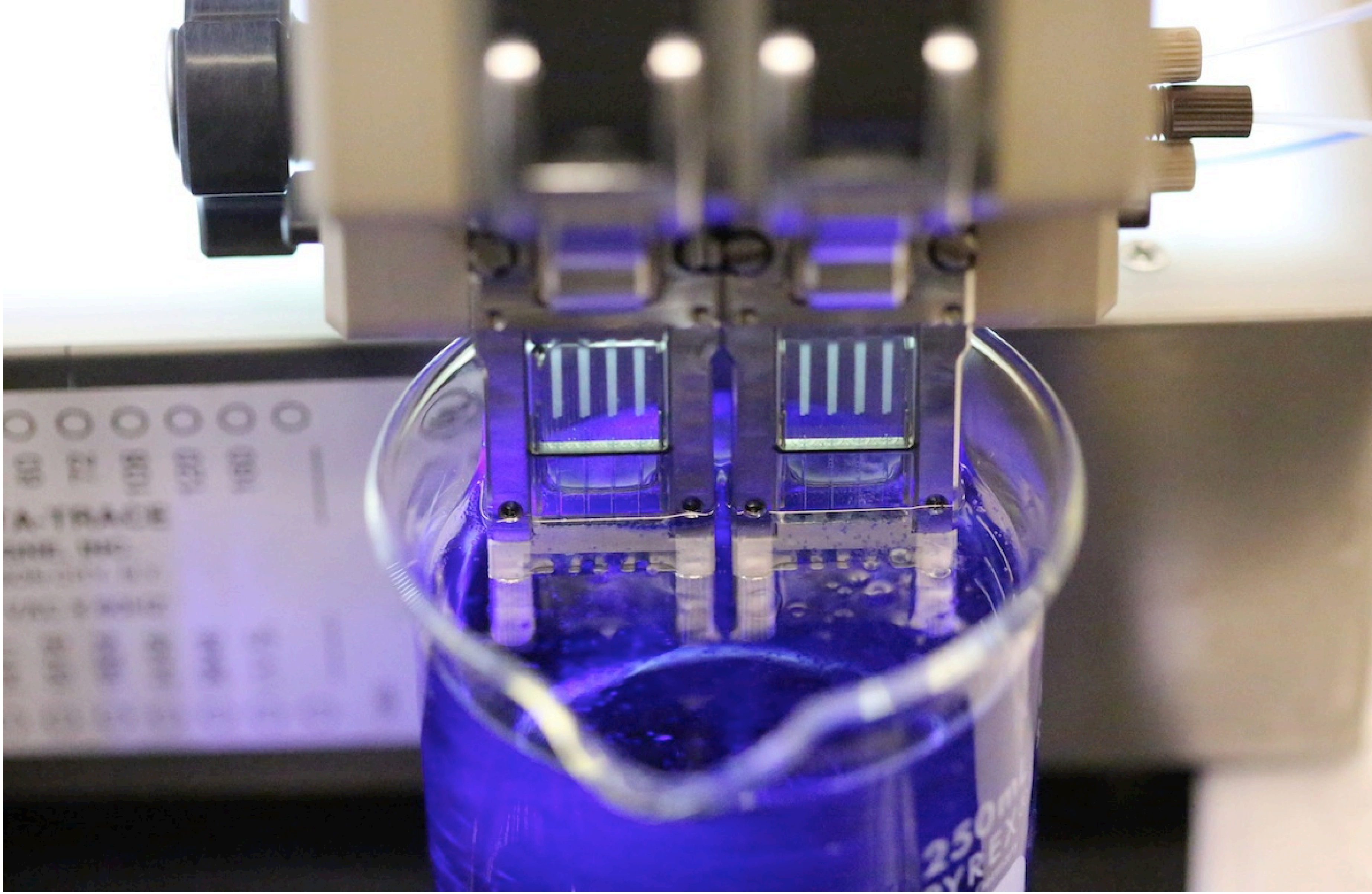


Etched glass chips from Dolomite Microfluidics

Tandem-Step chips developed at Harvard

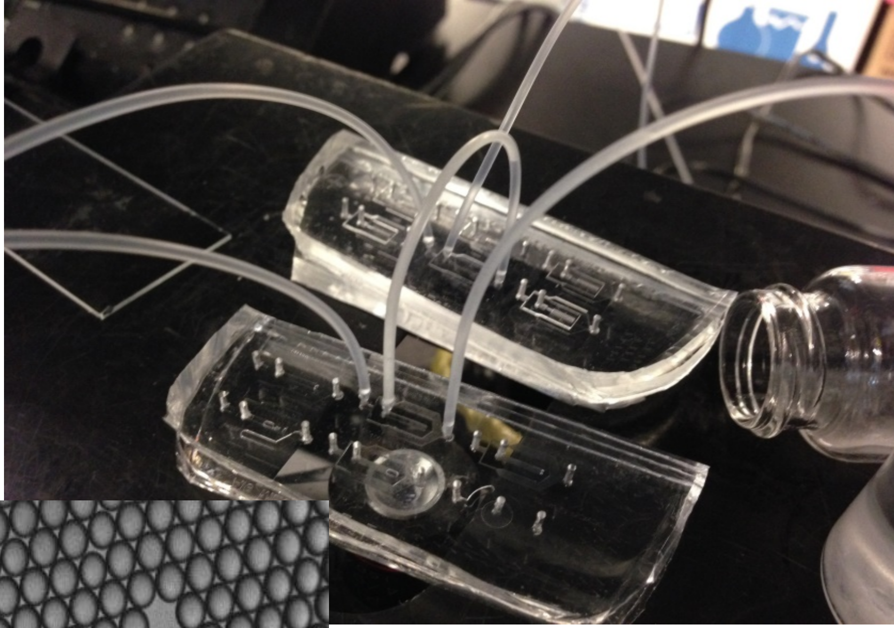


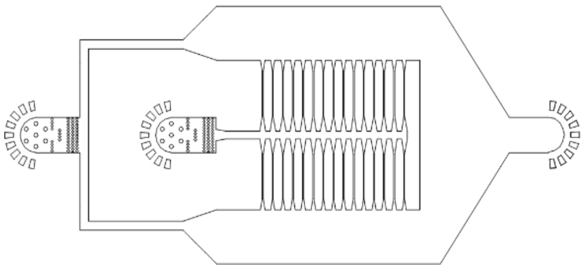
# Some success with 1st-generation multichannel chips

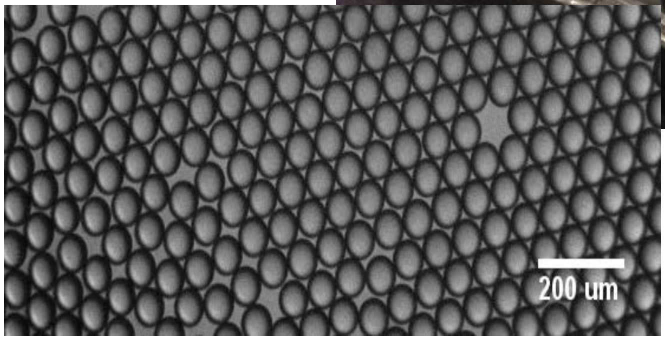


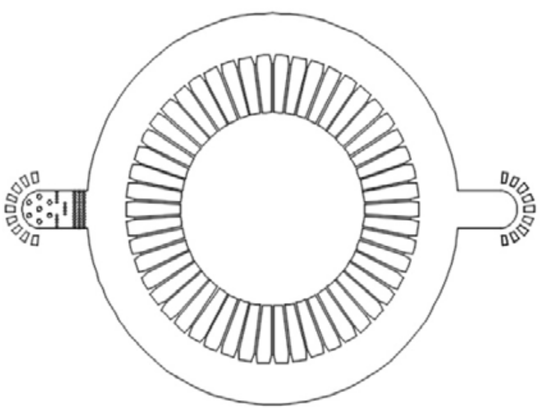
Two 4-channel chips producing capsules in parallel.

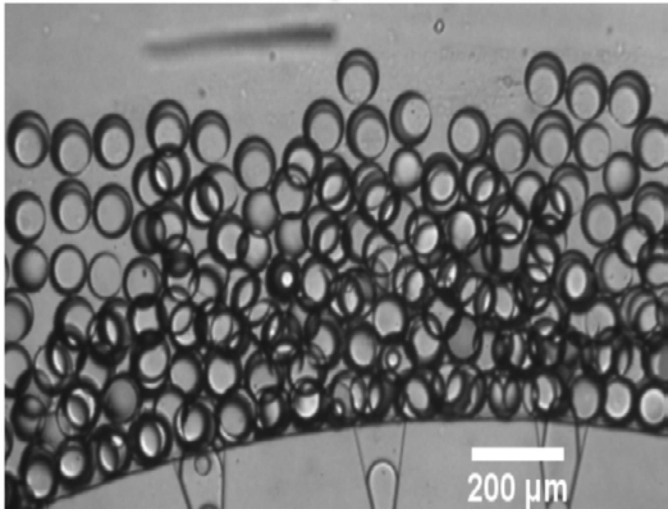
# Scale-up alternative:
# Tandem Step Emulsification









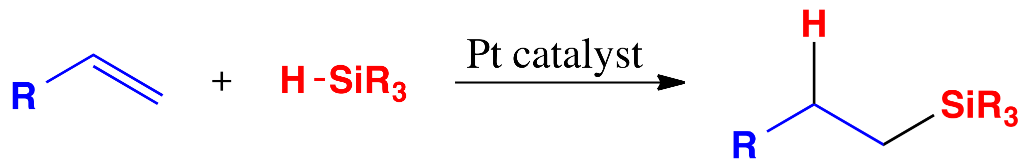
# Tandem Step Emulsification (Oil in Water)

# Challenge: capsule curing in the presence of amines

**Current shell material:** Semicosil 949UV, Wacker Chemie AG

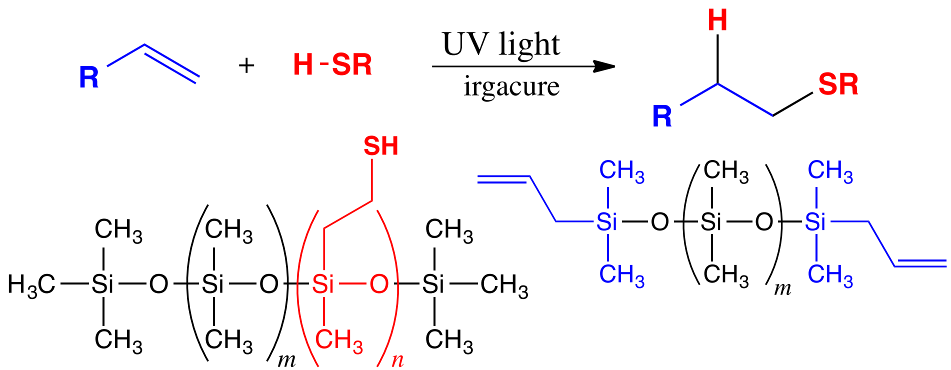
- Propriety silicone rubber blend (likely polydimethyl siloxane; PDMS)
- UV curable (likely UV-activated cross-linking through hydrosilation chemistry)

Hydrosilation:

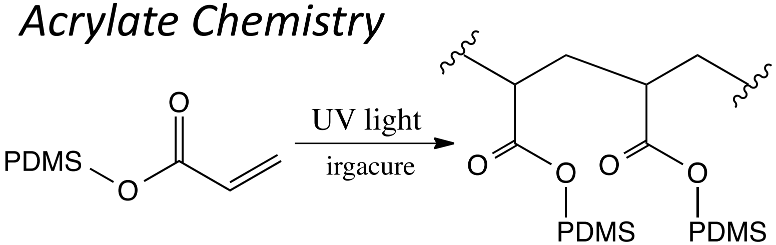



## Proposed alternatives

*Thiol-ene Click Chemistry*

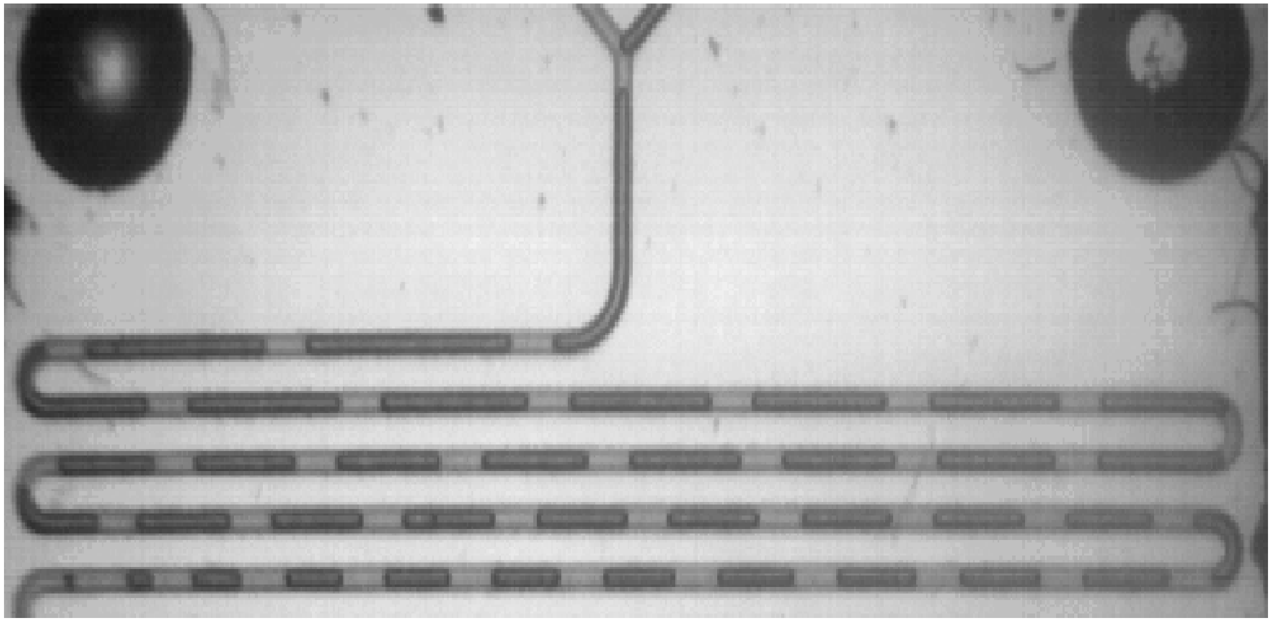


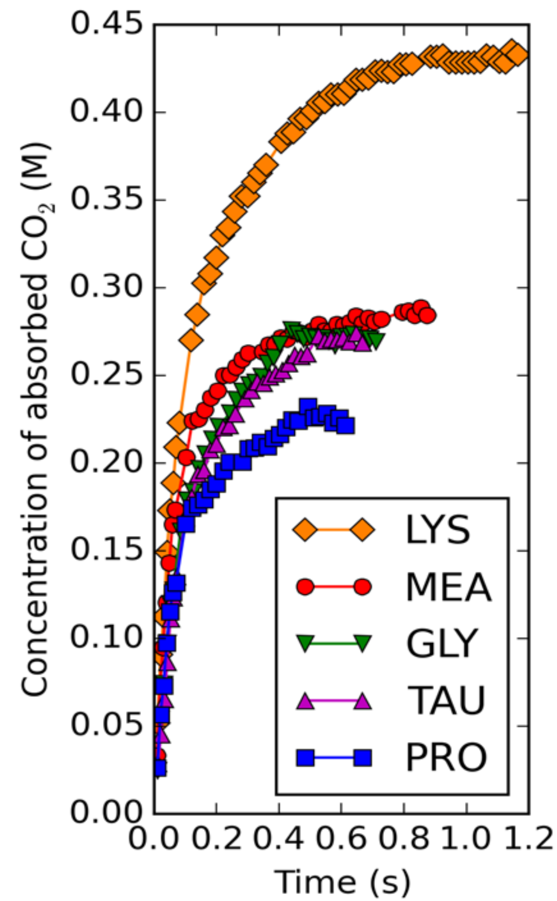

*Acrylate Chemistry*



# Challenge: determine solvent properties from small sample volumes.

Microfluidic characterization of $CO_2$ absorption solvents

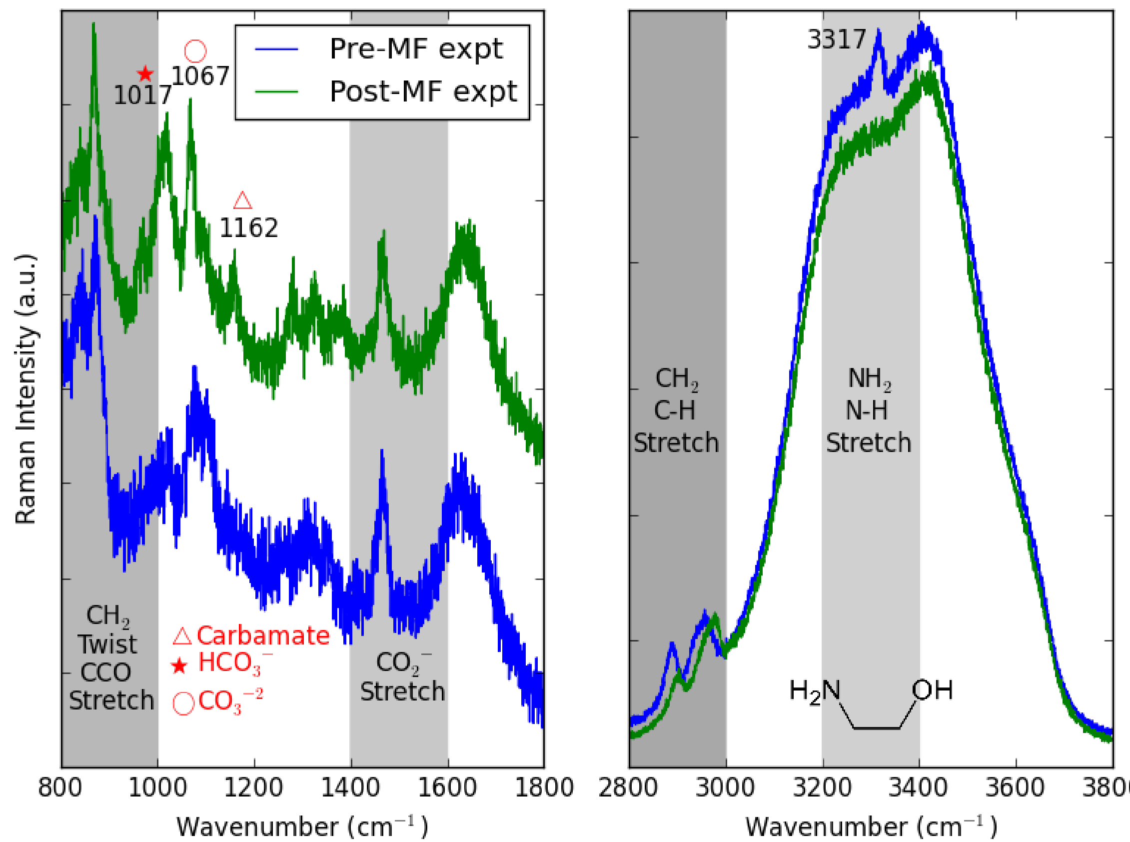





- Image analysis of gas bubble size vs channel distance provides uptake data
- Different solvents show different capture performance

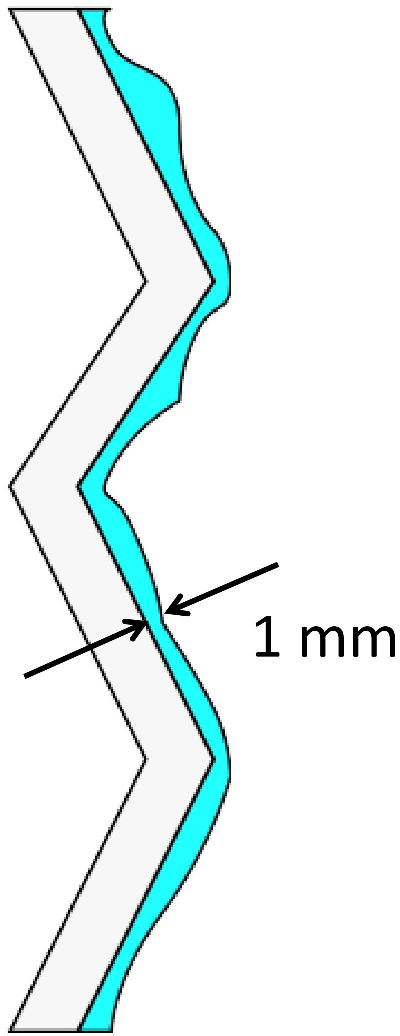
# Raman spectroscopy characterization of amino acid solvent $CO_2$ capture

- Raman spectroscopy can identify carbamate, bicarbonate, and carbonate species
- We see disappearance of reactants and formation of products




Potassium lysinate before and after $CO_2$ capture

# Improving absorber packings



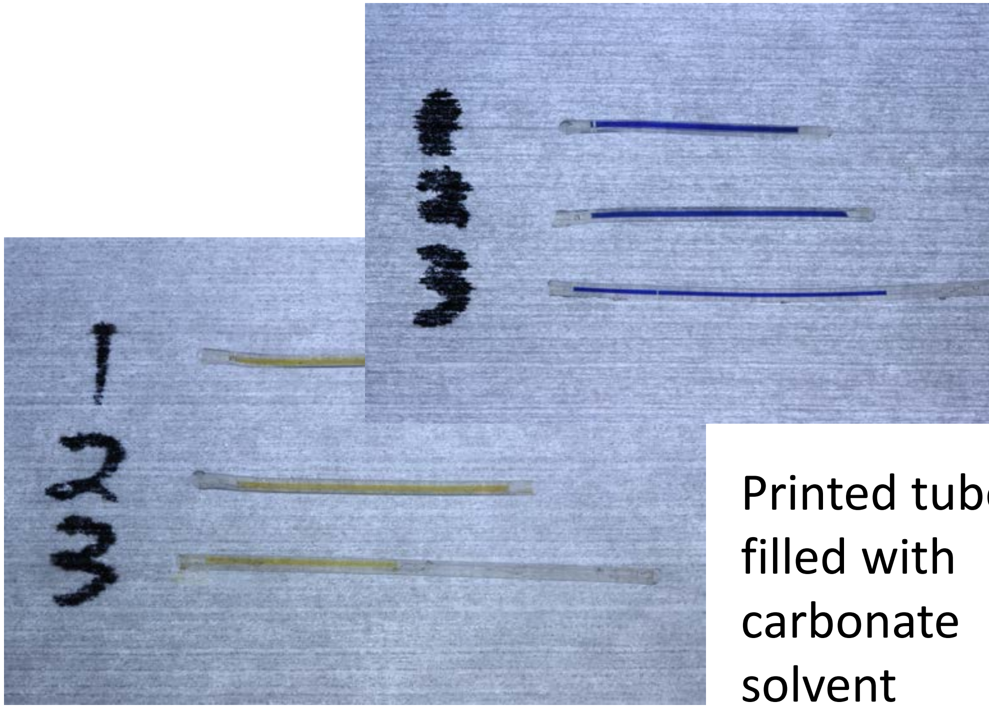

**Challenge:**

overcoming the film thickness

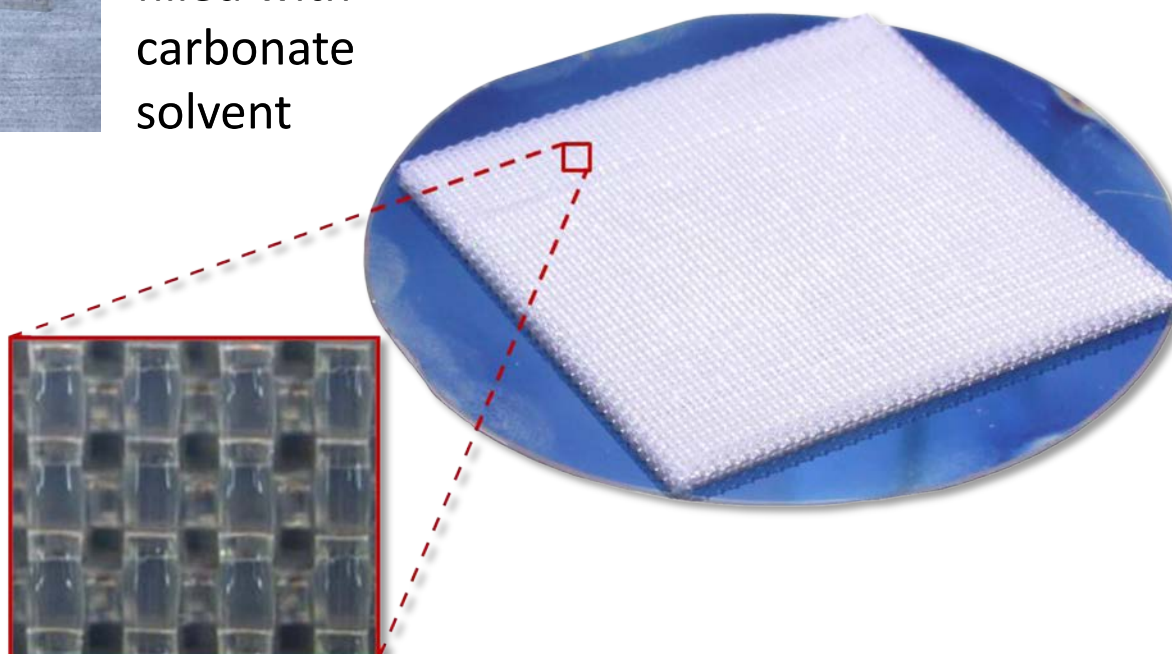
or

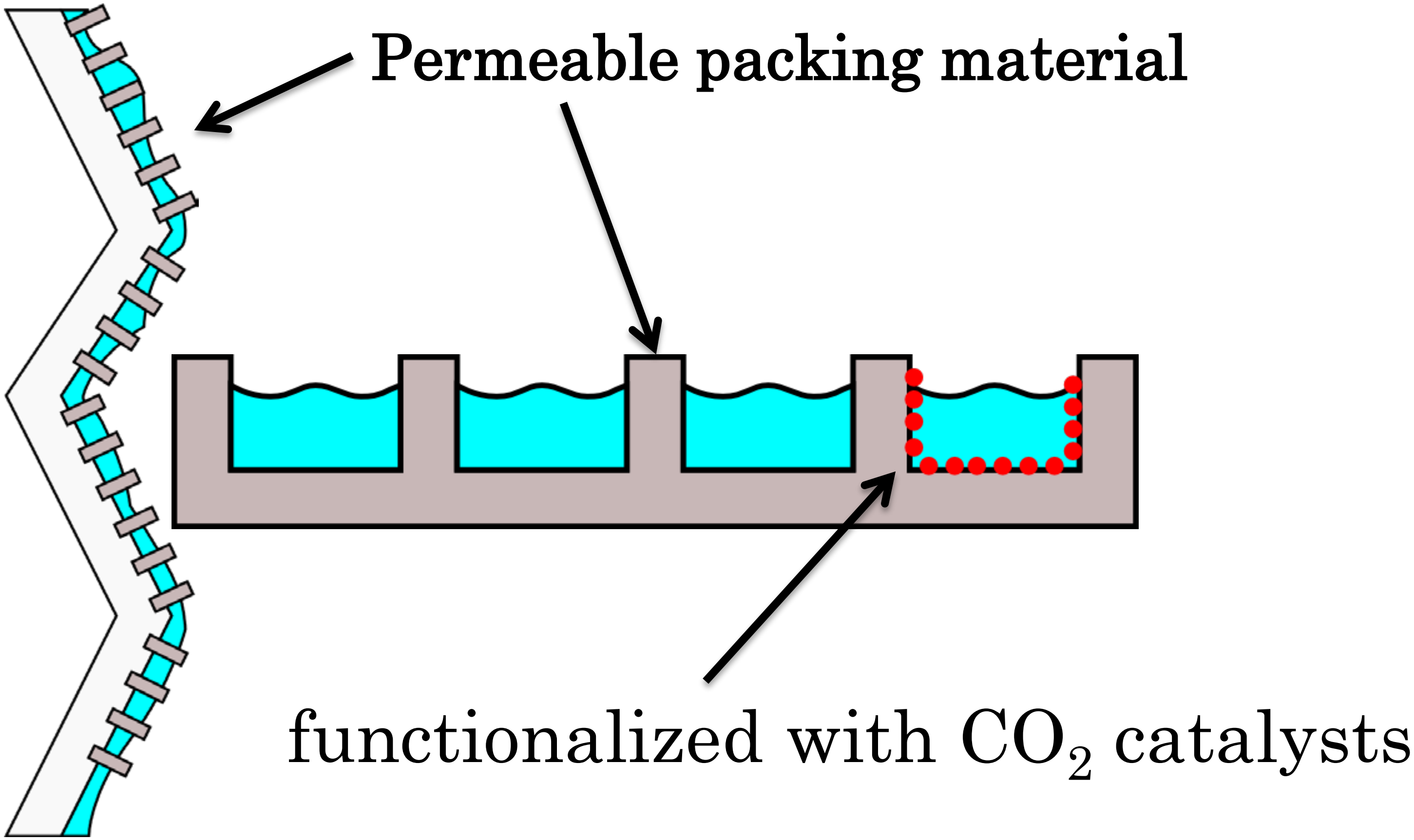
disrupting the boundary layer

# Core-shell Direct Ink Write



Printed tubes filled with carbonate solvent






→better surface area-to-volume and faster reaction in absorbers

# Acknowledgements

Lynn Brickett
Andy Aurelio

# Questions