Overview of Combi Methods for Soft Materials

NCMC-14: A DOE-EERE/NIST Joint Workshop on Combinatorial Materials Science for Applications in Energy

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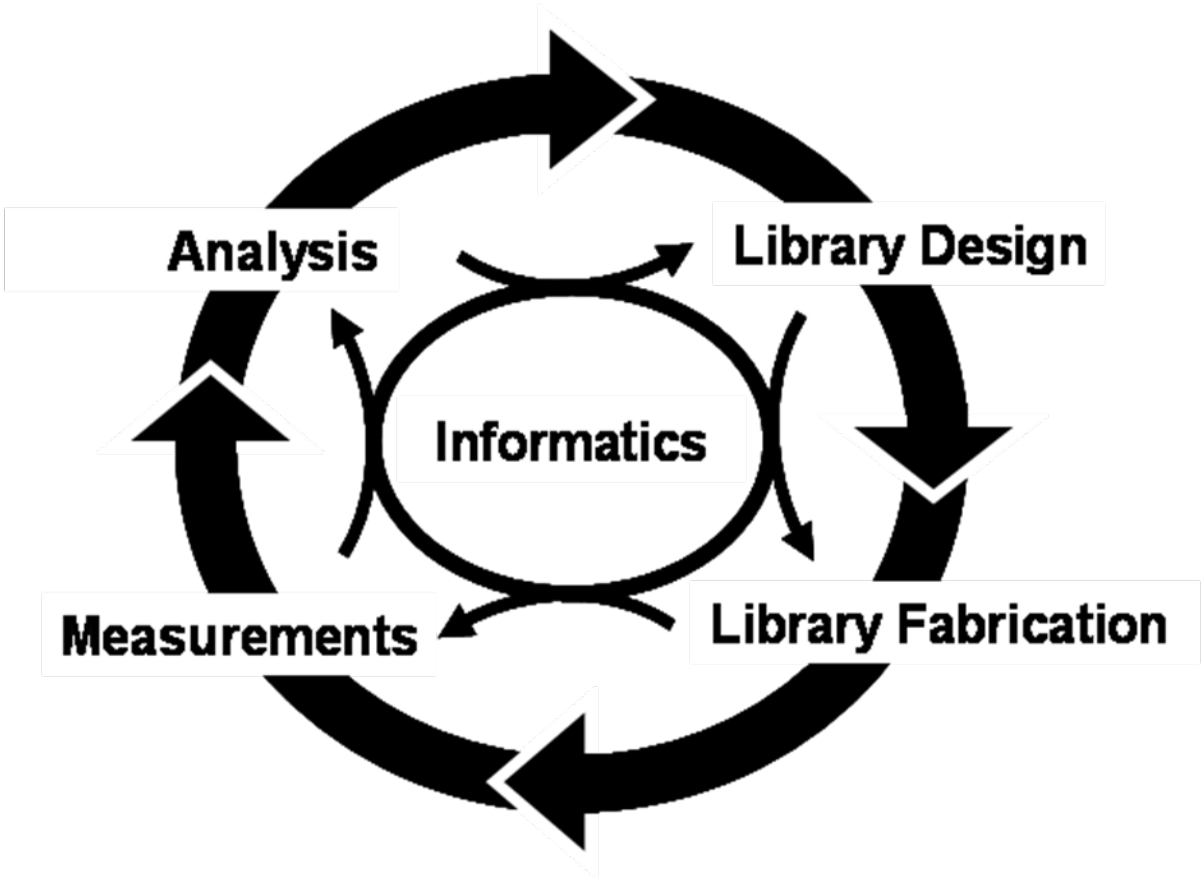
NIST Combinatorial Methods Center

Combi for Energy Related Soft Materials



- What can we leverage now?
- What do we need to progress?

Combi for Energy Related Soft Materials

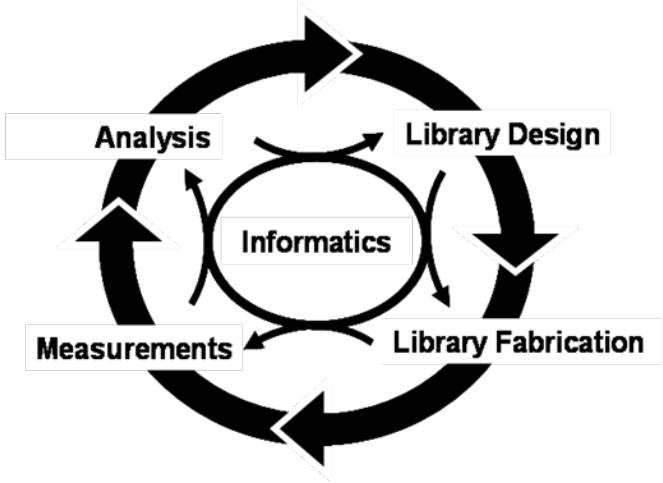
A brief outlook on:

Methods that can be leveraged

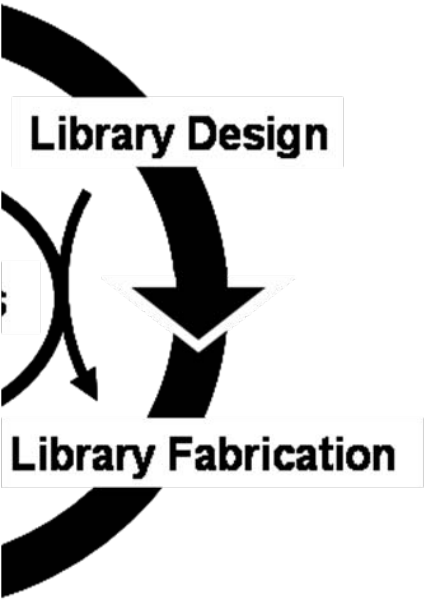
- Synthesis of custom materials
- Library approaches to complex mixtures
- High-throughput screening of materials properties and structure

Challenges to be met

- Library approaches to hybrid materials and devices
- High-throughput measurements of interface performance and reliability



Library Synthesis of Custom Molecules



Custom Soft Materials for Energy

- Fuel Cell Membranes
- Storage and sequestration
- Organic Photovoltaics
- Device Packaging
- Sustainable Replacements

Opportunities

- New synthetic routes that create complex molecule functionalities and architectures

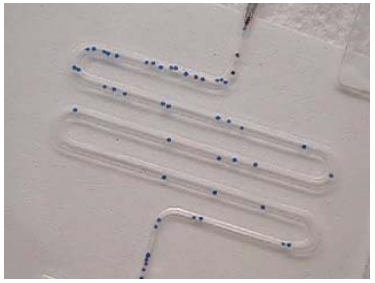
Needs

- Approach nearly endless molecular diversity
- Synthesis approaches that combine functional moieties
- Library approaches to materials optimization

Library Synthesis of Custom Molecules

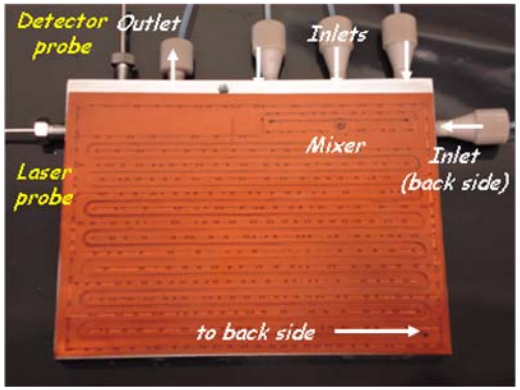
Automated Parallel Organic Synthesis

- Adapted from pharma and catalysis research
- Accommodate rigors of higher temperatures, pressures for organic reactions
- 10s of parallel reaction vessels
- Small Molecules and Polymers
- Commercial systems widely available

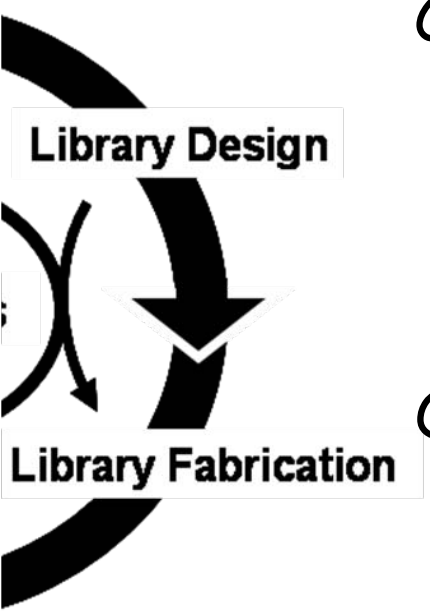


Continuous Flow Microreactors

- Adapted microfluidic technologies
- Systematic molecule synthesis
- Organic solvent compatibility
- Higher temperatures
- Integrated measurements
- Small volumes accommodate expensive components
- Progress towards scalability



Library Approaches to Complex Mixtures



Complex Soft Materials for Energy

- Fuel Cell Membranes from Blends
- Organic Photovoltaics
- Device Packaging
- Sustainable Replacements

Opportunities

- Formulation of soft materials by blending multiple components
- Tailored morphologies, combined functionalities

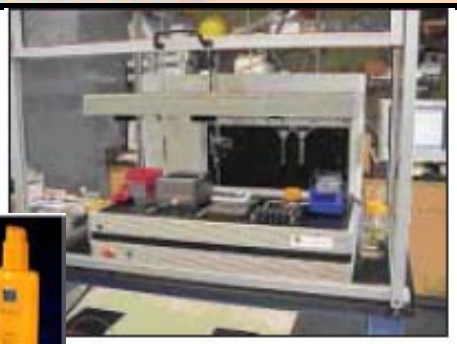
Needs

- Higher viscosity mixtures for e.g. polymer blends
- Particulate and powder handling
- More complex processing steps required
  - Film and membrane formation
  - Closer to industry fabrication

Library Approaches to Complex Mixtures

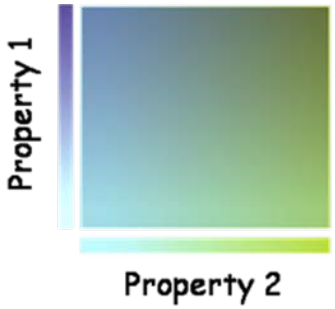
Liquid Handling Robotics

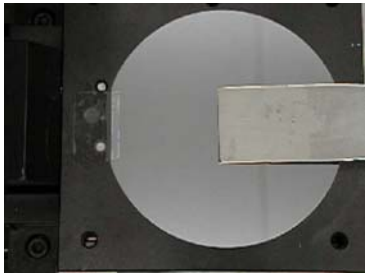
- Adapted from bio and pharma sectors
- Well established commercial technologies
- ~100 of milliliter-scale vessels
- Mixing and order of addition processing
- Solvent mediated; lower viscosity

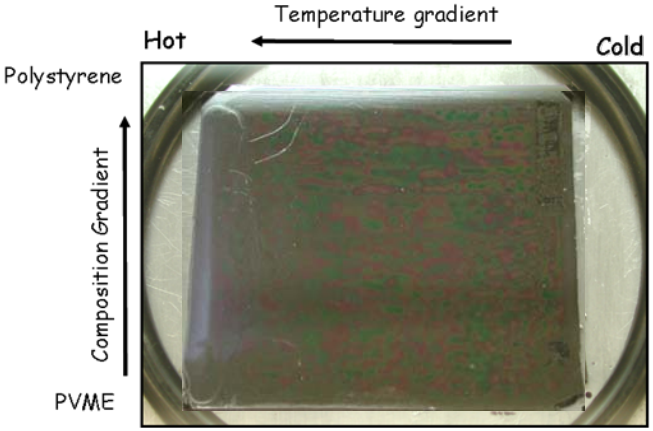


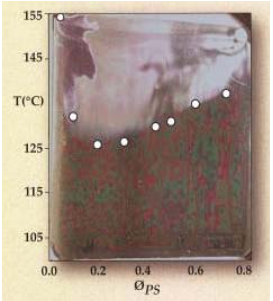
Gradient Film Methods

- Inspired by codeposition methods for inorganic materials
- Enables binary and ternary phase diagram library designs natural to materials scientists
- "Self Reporting" of phase fields and critical phenomenon
- Can be difficult for soft materials







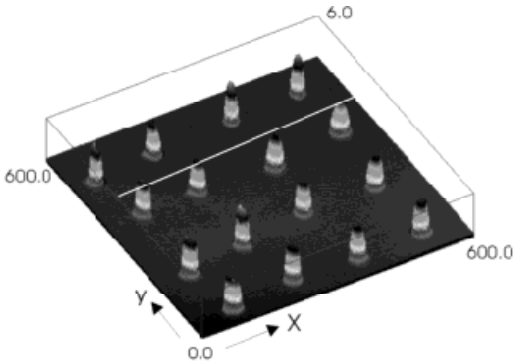


Library Approaches to Complex Mixtures

Next-Generation Dispensing Technologies

Inkjetting

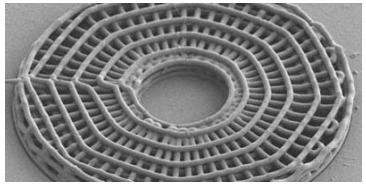
- Picoliter volume resolution
- Routine for small molecule solutions
- Difficult for macromolecules / higher viscosity
- Some progress in on-demand mixing



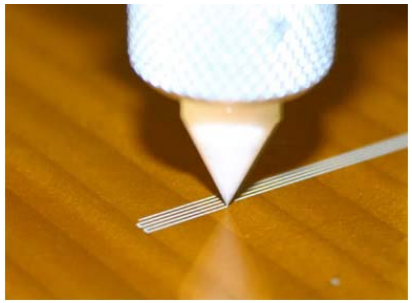
de Gans &Schubert LANGMUIR 20(18) 2004

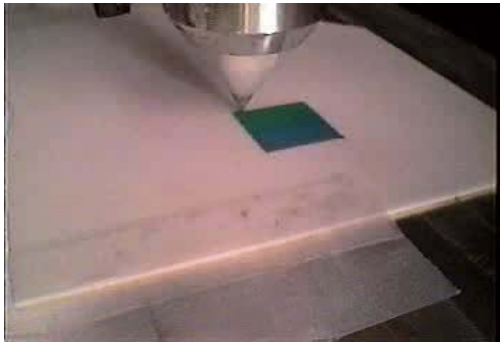
Direct Write Techniques

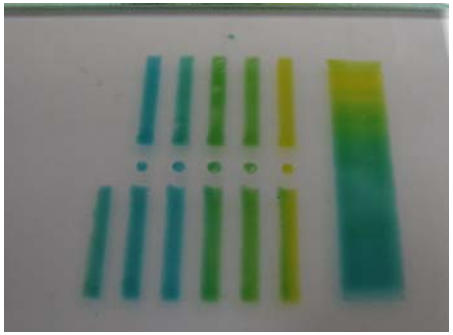
- Adapted on-demand fabrication methods
- Resolution: ~50 μm spatial, ~μl volume
- High viscosity fluids: blends and melts
- Complex structures
- On-demand mixing for combi arrays



DOE Materials Research Cluster
Programming Function via Soft Materials



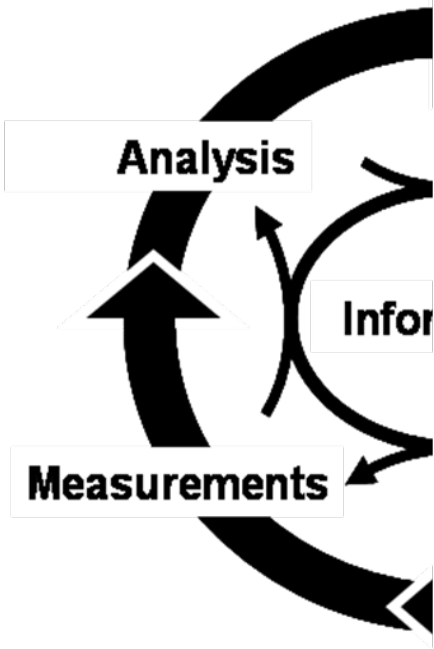




nScrypt Inc

HT Measurements of Properties and Structure

Soft Materials for Energy:



Structure Measurement Needs

- Hierarchical structure – nm to mm
- Polymer and Network Chemistry and Architecture
- Thin Film and Multilayer
- Surface and Interface
- Porosity

Properties Measurement Needs

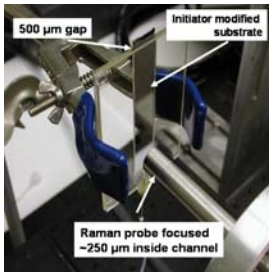
- Thermal
- Electrical
- Mechanical
- Phase Behavior

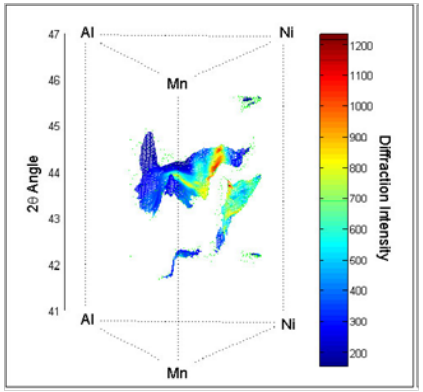
HT Measurements of Structure and Properties

HT Measurements Soft Materials Analysis

Chemical Structure

- Fiber optic Raman and IR Probes
- IR Microscopy



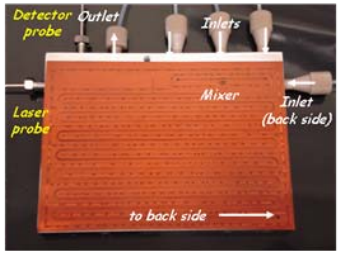


Materials Structure

- Automated OM and AFM
- X-ray scattering and diffraction

Solution Properties and Coil Size

- Fiber Optic Dynamic Light Scattering
- Parallel GPC

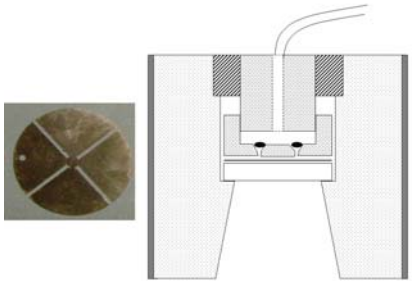


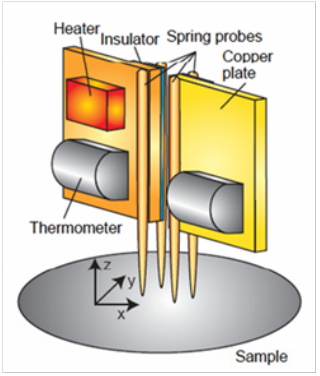
Thermal Properties

- Automated TGA and DTA

Mechanical and Rheological Properties

- Automated DMA
- Parallel and Miniature Rheometry





Electrical Properties

- A variety of automated probe stations

Combi for Energy Related Soft Materials

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Challenges to be met

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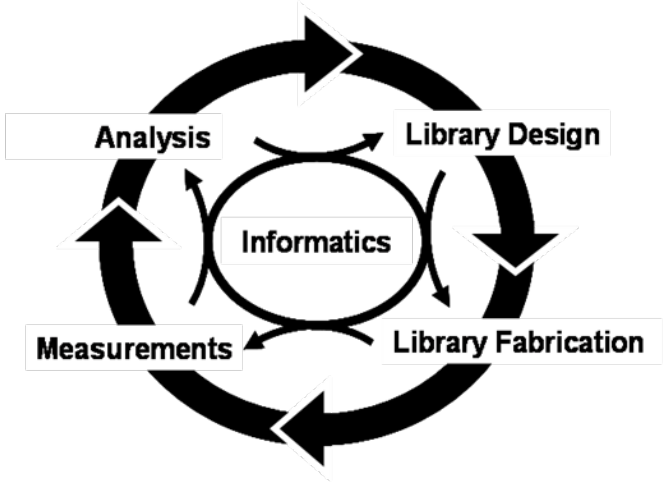
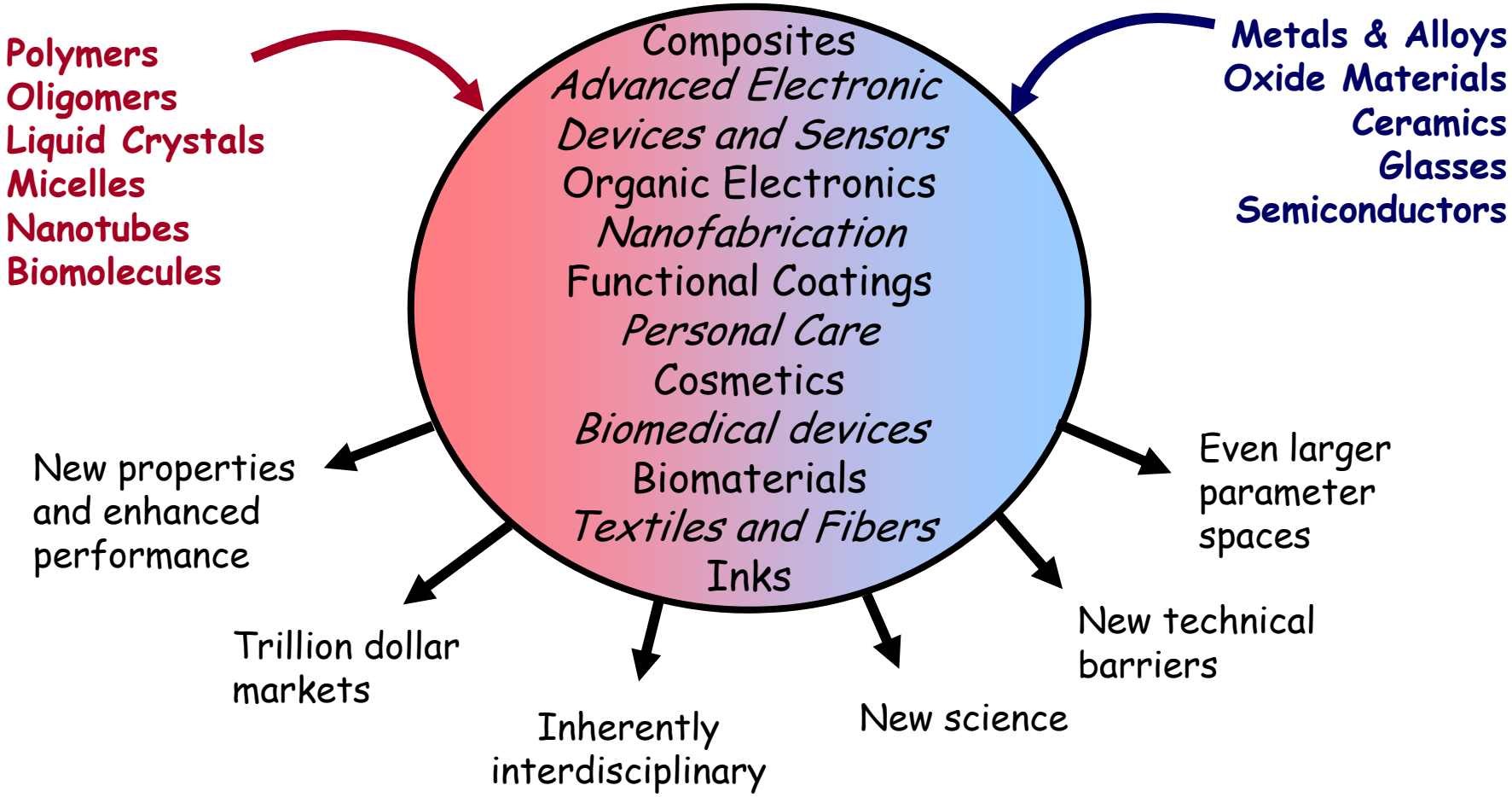
- High-throughput measurements of interface performance and reliability



Hybrid Materials Systems

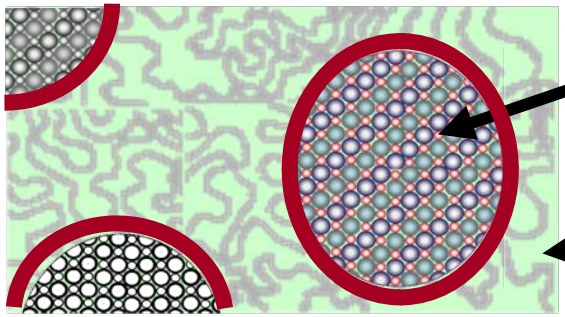
Emerging energy materials and devices often combine one or more disparate classes of materials.



Design Parameters in Hybrid Materials

Particle+Matrix Systems

Bulk Dispersion



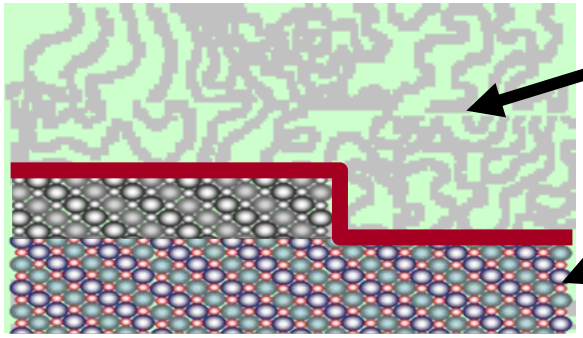
One or more particle types
- Composition, porosity
- Size, shape, polydispersity
- Loading, distribution, orientation

Homo- or Hetero-geneous matrix
- Molecular/Formulative composition
- Molecular structure

Coatings and Devices

May have multiple layers

Planar Geometry



Homo- or Hetero- geneous layer
- Molecular/Formulative composition
- Molecular structure
- May itself be laden with particles

Homo- or Hetero-geneous substrate
- Composition
- Topographic and chemical patterning

Variable space is huge, but performance targets may constrain on or more components…

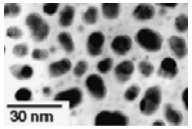
Disparate materials demand interfacial engineering:

Dispersion • Orientation • Adhesion • Wetting • Stability • Transport…

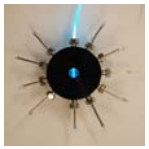
First Challenges to Hybrid Materials Combi

The same challenges inherent to extending combi to any new materials set

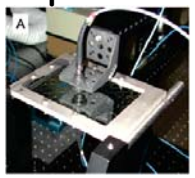
HT Microscopy



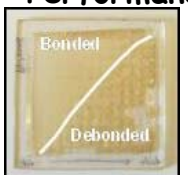
HT Scattering

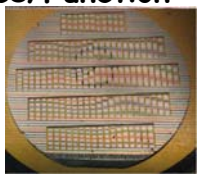


HT Spectroscopy

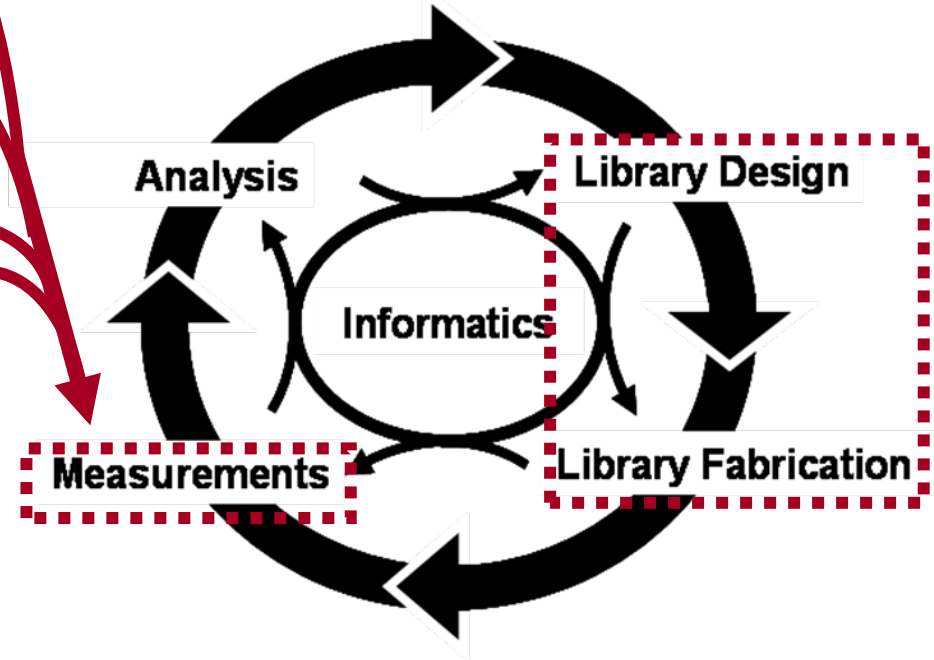


Performance/Function

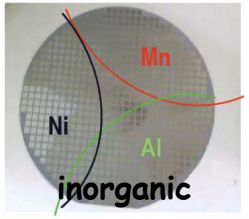


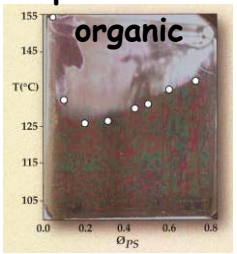


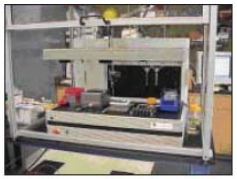
Combi of Complex Materials



Composition Spreads

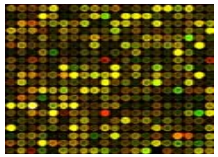






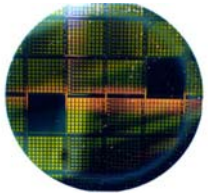
organic

Combi chem



inorganic

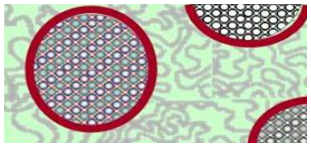
Device libraries

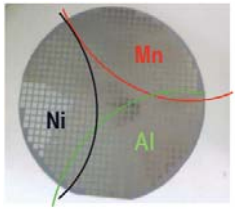


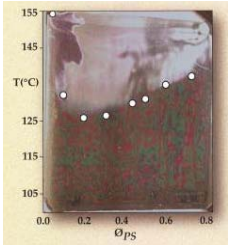
Challenge: Library Fabrication

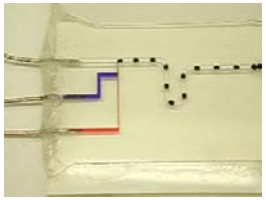
Particle + Matrix Libraries

- Spreads in composition, size, shape
- Yields sufficient for 2%-10% loading into matrix specimens
- Leverage planar inorganic composition spreads?
  - As a means of particle library fabrication
  - As a means of particle composition screening
- How to introduce particles into matrix libraries?
  - Thin film deposition techniques?
  - Microfluidics?
  - More traditional parallel compounding?



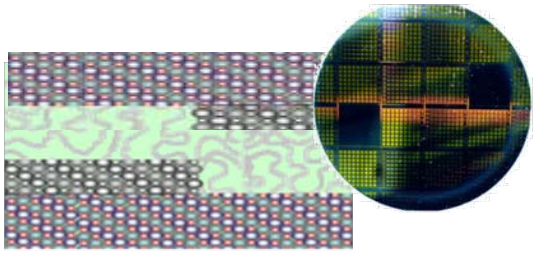


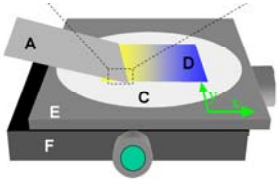


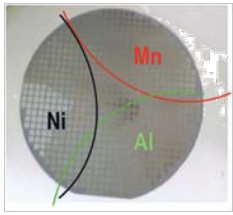


Complex Materials Multilayers and Device Testbeds

- Individual aspects of thin film combi methods already well developed
- Alternating and co-deposition of organic and inorganic layers
  - Combining solution- and (e.g.) sputtering- based methods
- Microscale patterning of both kinds of layers
  - Combining traditional and "Soft" Lithographies

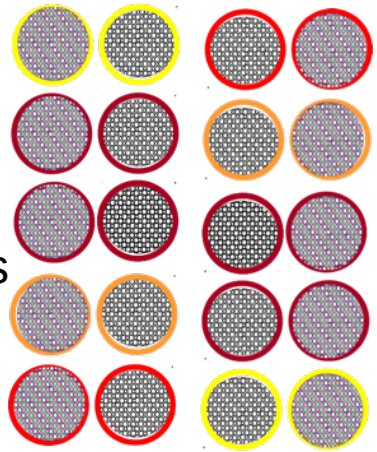






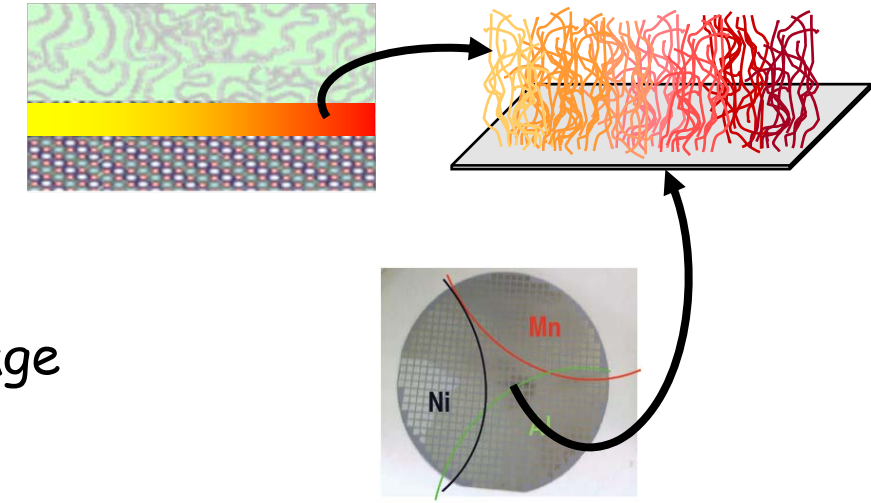
Challenge: Libraries for Interfaces

Surface functionalized particle libraries



- Bio-sector has produced several schemes for combinatorial particle labeling with various ligands
- Combi functionalization for organic and polymer target matrices is less developed
- Same constraints as unfunctionalized particle libraries: sufficient yield and amenable compounding route
- Can functionalized flat libraries act as a screen for the harder case of functionalized particles?

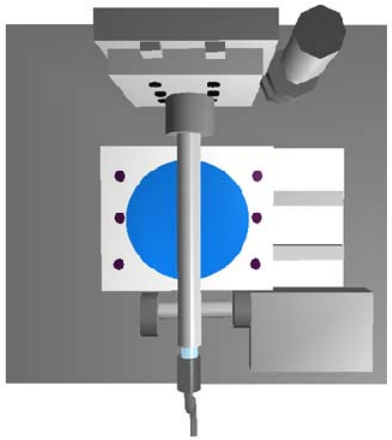
Planar libraries of surface functionalization

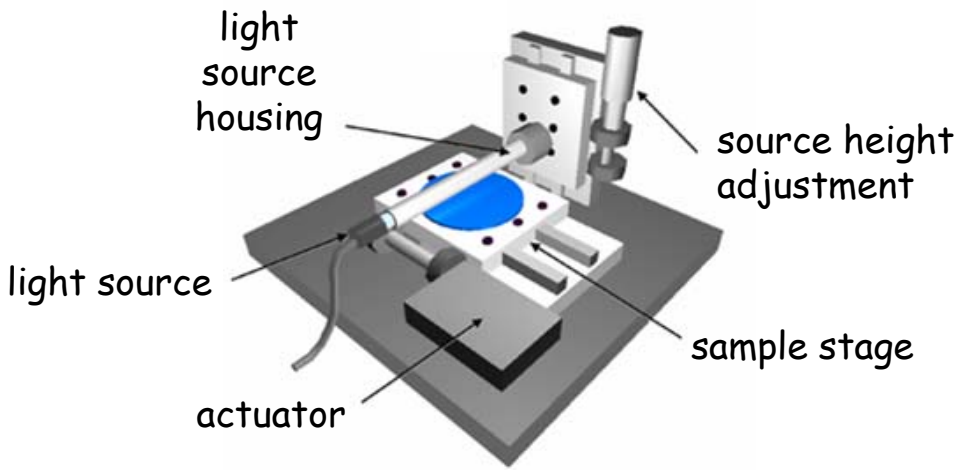


- For multilayer and device combi
- Versatile with respect to substrate
- Patterned – soft lithography, leverage biosector
- Systematic roughness variation

Example: Light exposure gradients

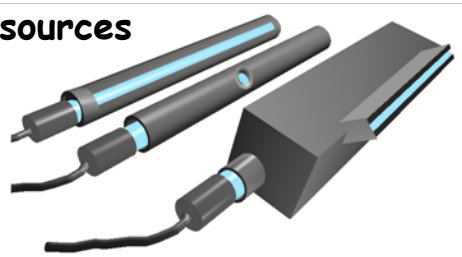
NIST Gradient Light Exposure Device





Light source appliances

For wand sources

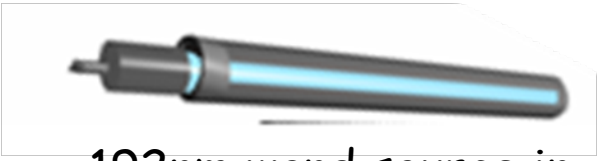


For flood sources

- Gradients using a variety of flood and wand-type light sources
- Gradual, Well Behaved Libraries:
  - Surface energy/hydrophobicity
  - Film Stability and Nanostructure
  - Bio-functionality
  - Photopolymerization
  - Photo-aging and degradation
  - Photoresist processing

Berry, Stafford, Pandya, Lucas, Karim, Fasolka, Review of Scientific Instruments 78(7), 072202, 2007

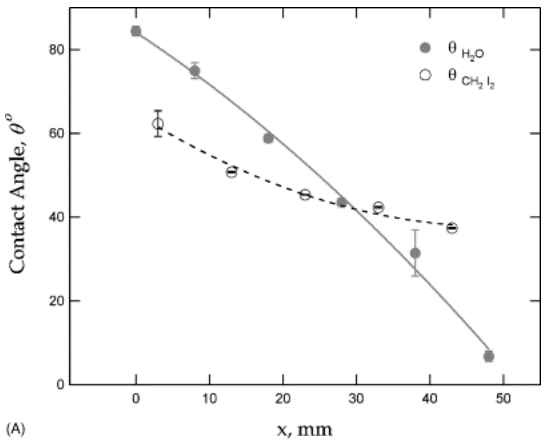
Graded UV-Ozonolysis

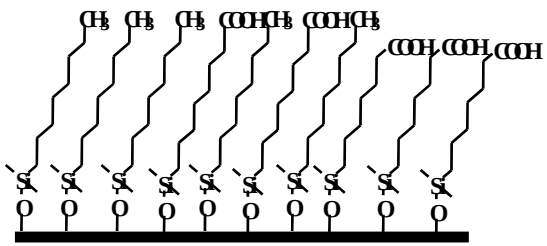


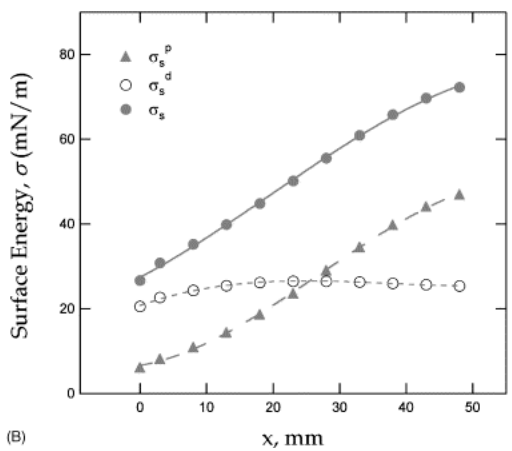
192nm wand source in slit aperture housing

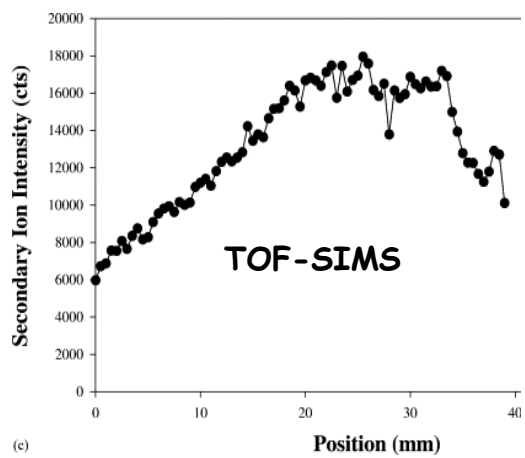
"Surface Energy" Gradient

Library Range:
20-78 mJ/m^2

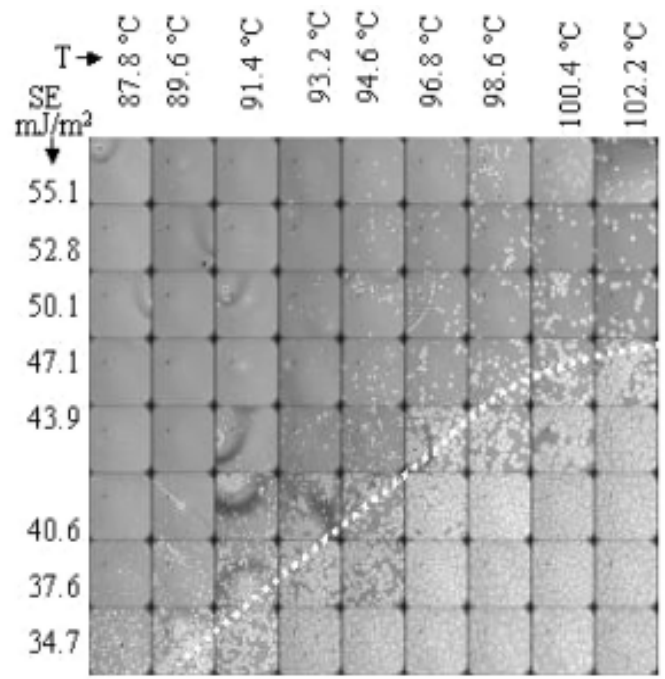








Dewetting and film stability



Roberson, Fahey, Sehgal, Karim, Applied Surface Science **200**, (2002)

Ashley, Karim, Douglas, Langmuir, 21, (2005)

Surface/Interface Chemistry Libraries

End-grafted polymers are a robust means to functionalize surfaces

- Covalent bonding
- Enhanced surface coverage
- Enhanced end group expression

} "Brush Effect": volume exclusion, elongated coils

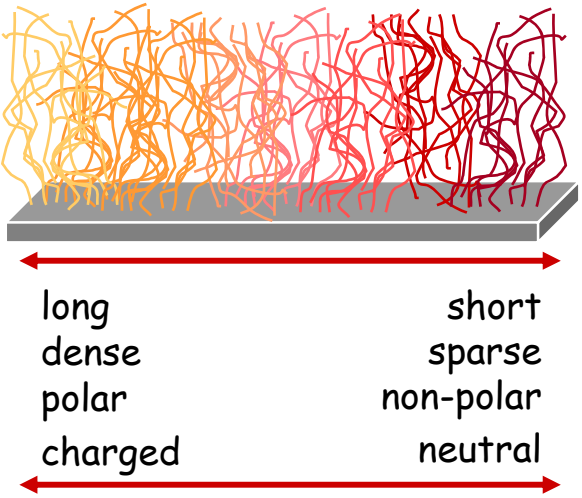
S. T. Milner, *Science* 251, 905 (1991)

New controlled synthesis routes enable grafted polymer with designed chemistry and architecture

Matyjaszewski, et al, *Macromolecules*, 1999
Huang, *et al*, *Macromolecules*, 2002

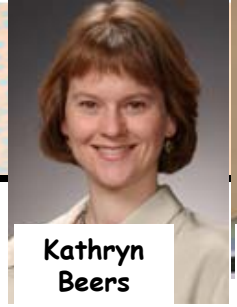
NIST brush libraries enable:

- *Rapid Hypothesis Screening*: Map the molecular parameters thought to govern behavior in a single specimen
- Design, optimization and application of grafted polymers
- Our next generation surface chemistry gradients

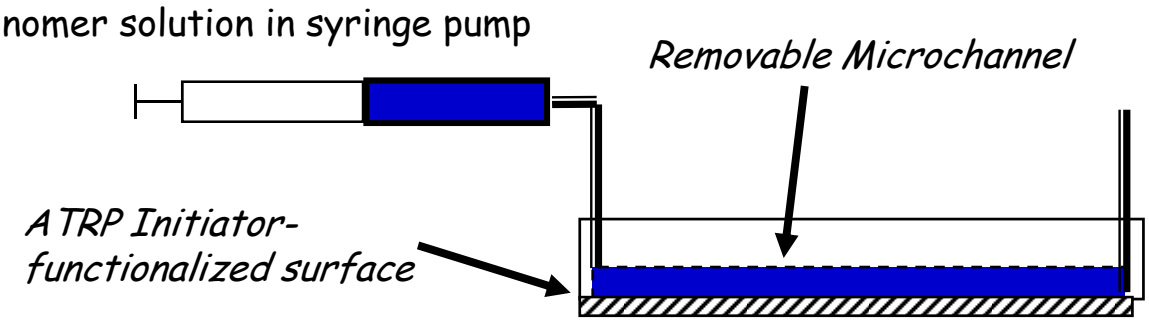


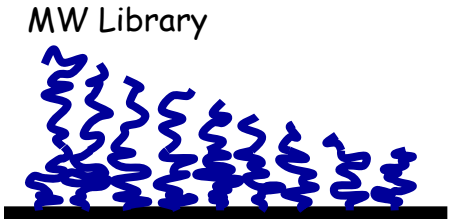
See also: Tomlinson, M. R.; Genzer, J. *Macromolecules* **2003**, *36*, 3449-3451.

Microchannel Confined Surface Initiated Polymerization (μSIP)



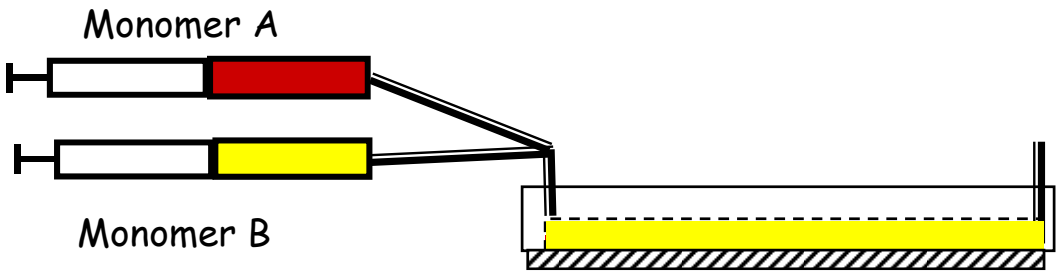
1)

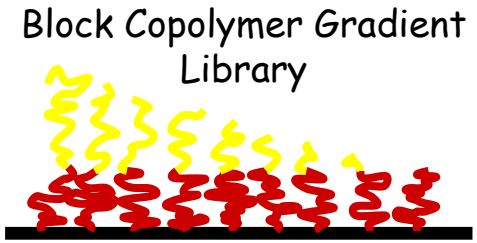




Xu, Wu, Mei, Drain, Batteas, Beers *Macromolecules* **2005** 38 (1):, 6.

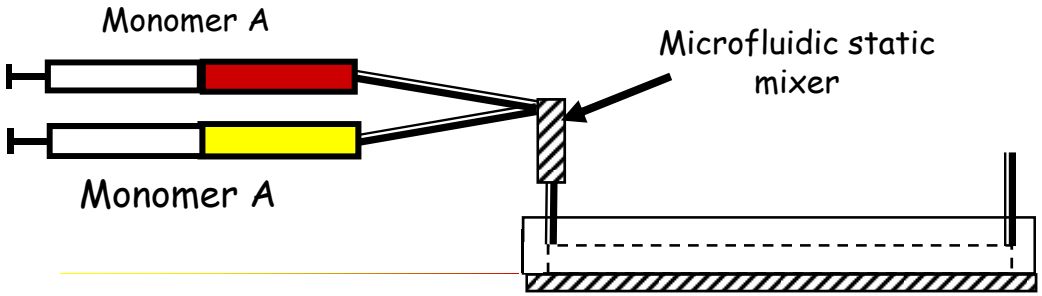
2)

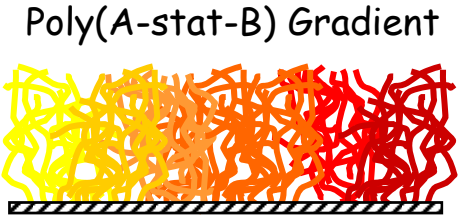




Xu, Beers, Fasolka et al, *Macromolecules* 2006, 39 (9), 3359 & *Applied Surface Science* 2006, 252 (7), 2529.

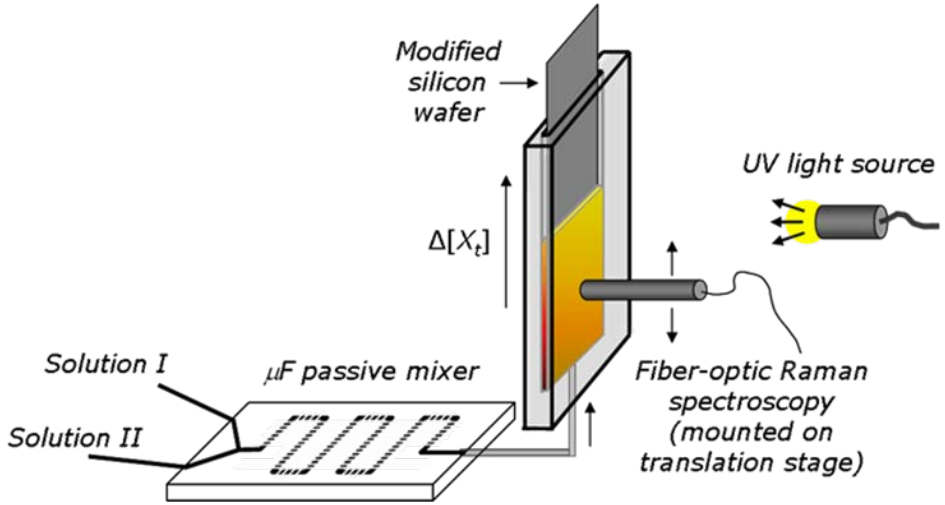
3)

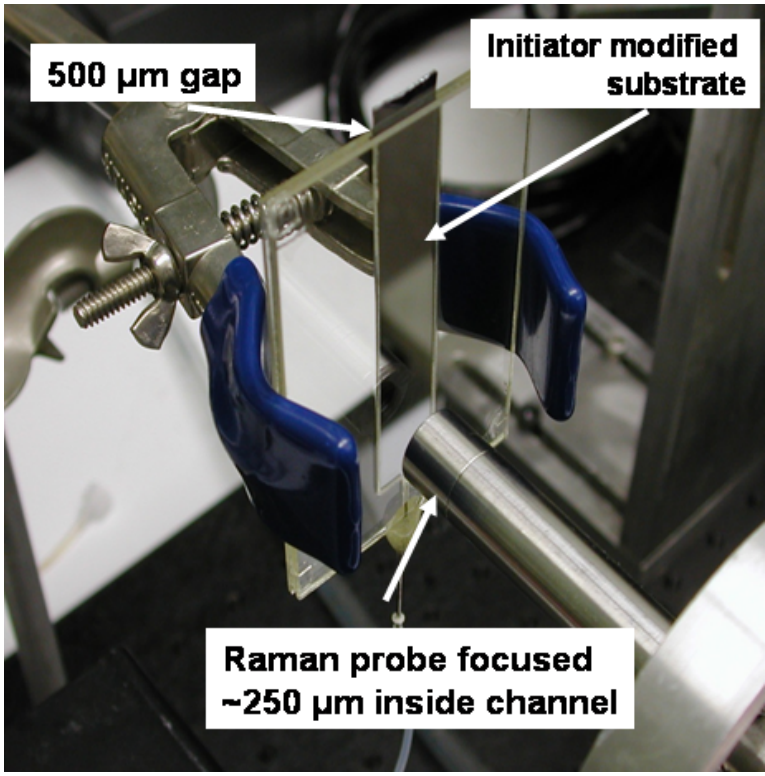


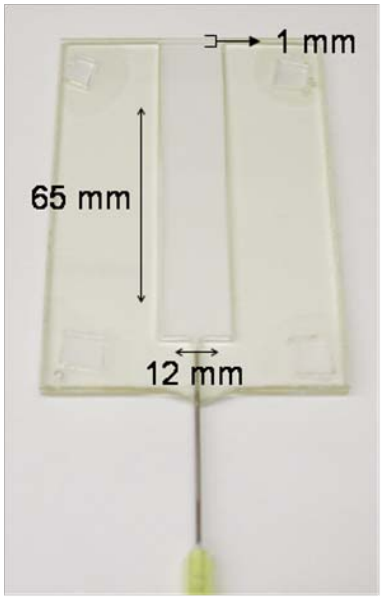


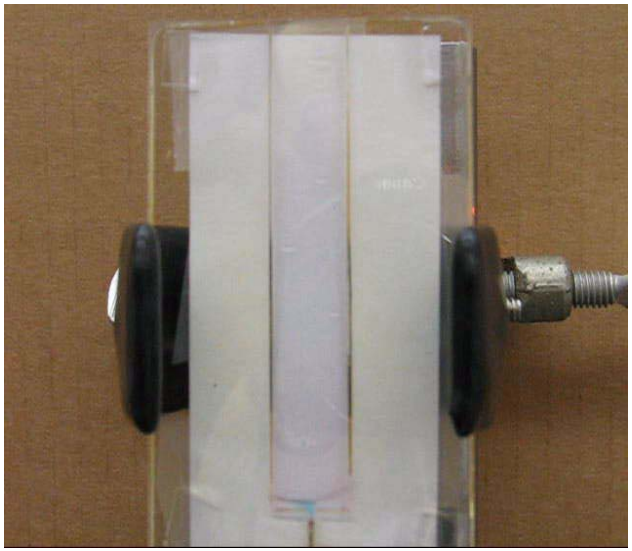
Xu, Wu, Beers et al, *Advanced Materials* 2006, 18 (11), 1427.

Solution Gradient Library Fabrication



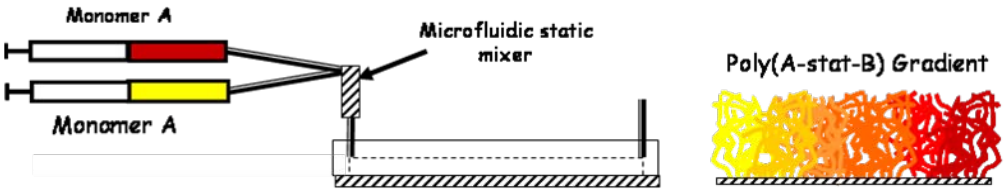




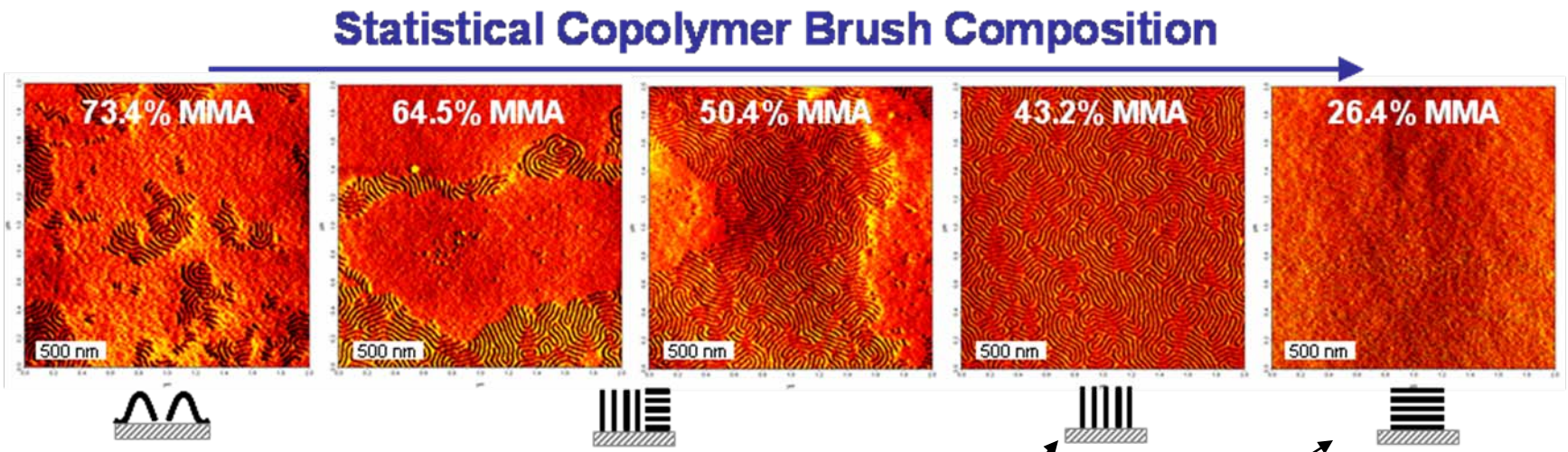


Thiolene resin and glass microchannel

Statistical Copolymer Libraries

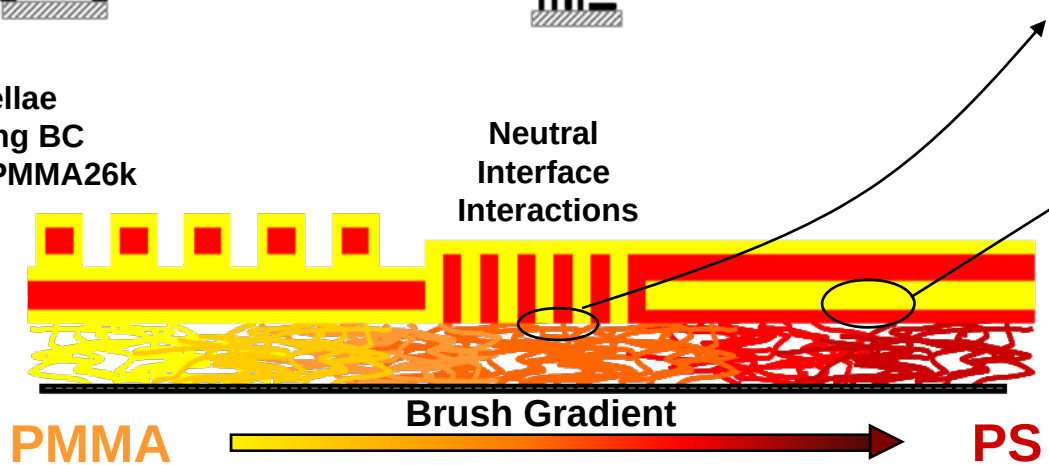


Platform for screening "neutral surface" hypothesis in thin film block copolymer self assembly



Lamellae Forming BC PS25k-b-PMMA26k

Neutral Interface Interactions

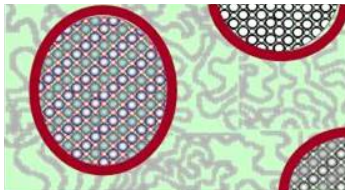


Other BC systems:

- PS-b-PnBMA
- PS-b-POMA

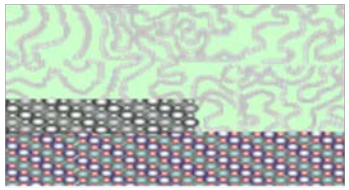
Key Measurements: Interface behavior and structure

A huge challenge:



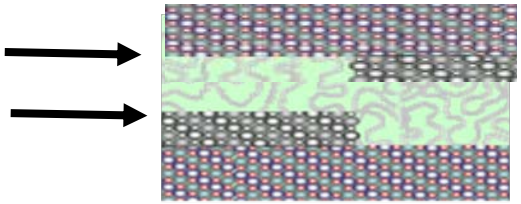
HT approaches to surface analysis

- X-Ray Photoelectron Microscopy
- Near-Edge X-Ray Absorption Fine Structure (NIST)
- Advanced SPM Techniques
  - Quantification of image data (NIST)



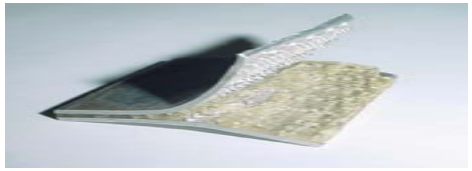
Structure of "buried interfaces"

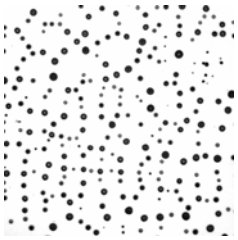
- Reflectivity?
- Sum Frequency Generation?
- Confocal microscopy?
- Clever sample preparation techniques?



Performance of interfaces

- Adhesion, wetting and stability
- Transport properties
- Barrier properties…
- Which interface is critical?



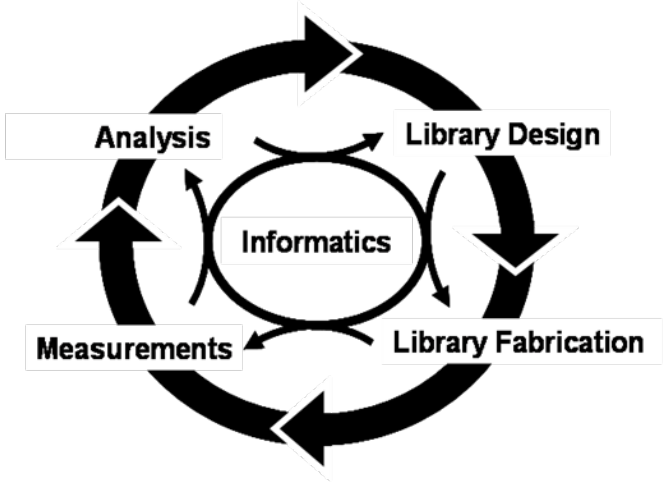


Combi for Energy Related Soft Materials

A brief outlook on:

Methods that can be leveraged

- Synthesis of custom materials
- Library approaches to complex mixtures
- High-throughput screening of materials properties and structure

Challenges to be met

- Library approaches to hybrid materials and devices
- High-throughput measurements of interface performance and reliability