Nanomaterials and Biomimetics Research in Chemical Engineering

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**Objective:** Achieve spatial control in wettability

Chaudhury & Whitesides
*Science 256*, 1539 (1992)

**Source** = chlorosilane/paraffin oil mixture

Vapor flux controlled by chlorosilane/paraffin oil ratio

**Tunable molecular gradients**

**Objective:** Utilize gradient substrates in templating

- Microscopic (discrete)
- Macroscopic (continuous)

**Dry PAAm thickness before Au dip (nm):**

- 3-16 nm

**Au particles**

**Position on the substrate, x (mm):**

- 10 15 20 25 30 35 40 45 50
- 3 4 5 6 7 8 9 10

**Particles per µm²:**

- 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50
- 100 200 300 400 500 600 700 800 900 1000 1100

**Langmuir**

*The ACS Journal of Surfaces and Colloids*

*Substrate-Bound Nanoparticle Assemblies with a Continuous Number Density Gradient (see p. 54)*
Tailored polymer synthesis

Objective: Use combi methods to synthesize novel polymer structures and motifs

Partial topics:
• kinetic of ATRP;
• block tunable copolymers;
• tunable polymer/nanoparticle dispersions.

**Material screening methods**

**Objective:** Use gradients in screening protein adsorption behavior

Adsorption of Au nanoparticles (Φ ≈ 16 nm) adsorbing onto PDMAEMA brush at different temperatures on silica.

Adsorption of proteins onto PHEMA molec. weight gradient (only a single sample is utilized!).

**Fibrinogen**
(conjugated w/ AlexaFluor-594, deposited onto PHEMA substrate, and incubated @ 4°C for 72 hrs)
Research interests of
Richard J. Spontak
Departments of Chemical Engineering
and Materials Science & Engineering

Nanostructured polymers
Block copolymer systems, physical gels, nanoporous media
Multifunctional materials used in dampening, separations & optics

Mesoporous media
High-pressure CO₂ as a benign, low-T route to nanoporous polymers
Lightweight materials for delivery, separations, low-k dielectrics

Polymer Nanocomposites
Impregnation and growth of metals and metal oxides in polymers
Robust materials for use in catalytic reactions and gas separations

Advanced Microscopy Methods
Quantitative transmission electron microtomography for use in quantifying volumetric characteristics at nanoscale resolution.
Energy-filtered TEM for high-resolution elemental imaging.
Environmental AFM for low-T characterization of soft materials.
Nanostructured Polymers

**Motivation:** Design and characterize novel nanostructured polymer systems that afford unique opportunities for property development.

Electron tomography

- Fe-containing block copolymer nanotubes
- High temperature-stable block copolymer gel

Mesoporous Media

**Motivation:** Develop viable and controllable process routes to ultrahigh-porosity materials that provide low-weight, high-strength and possibly surface-functionalized opportunities.

Surface-mediated thin-film foaming

Foaming of PMMA at low pressures & temperatures in liquid CO₂

*Polymer* 43, 5511 (2002)
“Inside-out” templating: Colloidal crystals replicated into structured porous materials

Velev et al. 

### Colloidal crystals:
- Maximal packing density and surface/volume ratio
- Maximal structural stability
- Interaction with light: diffraction, interference, scattering

### “Inverse opals”:
- Robust and self-sustained
- Uniform porosity and mass transfer properties
- Could be a full photonic bandgap material
“Inside-out" templating: Structured metallic films via colloidal crystals

Potential uses for nanocoatings

Photonics and optical
- IR filters and mirrors
- SERS sensor substrates
- Wave guides
  - Energy harvesting
  - Decorative materials

Electronic
- CVD alternative
- Low dielectric materials
- Conductive/ Semiconductive porous materials

Catalytic
- Uniform porous supports
Use of structured **metallic films** via colloidal crystals in chemical microsensors

- Cell holds 170 ml, response in < 3 min
- Excellent performance with chemical agents, LOD for cyanide = 10 ppb
- Revealed kinetic and spectroscopic effects of both fundamental and practical importance

Microstructures and Devices via Dielectrophoretic Manipulation and Assembly

“Photonic”: Optical devices

Biological: Sensors

Electrical: Interface on-chip circuits

Switchable crystals

Biosensors

Microwires

References:


Dielectrophoretic assembly of microwires from metallic nanoparticles

40 – 150 V AC
200 - 3000 Hz

Grounded

Single wire grown through gap
Dynamics of microwire assembly
High magnification, 8X speed

Hermanson, Lumsdon, Kaler and Velev
Predicting wire assembly in the presence of conductive object in the liquid

Self-centering of the wire **after** growth begins

Growing wires would spontaneously complete the circuit through the object

Experimental image

*Finite element electrostatic calculations using conformal triangles mesh (TriComp package)*
"Outside-in" templating:
Advanced structured particles templated by surface tension

Four droplets of various suspensions held on a fluidic chip

750 nL droplets containing

← red fluorescent latex
← gold nanoparticles
← white sulfate latex
← magnetic latex

Energized columns of electrodes