Self Assembly

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Summer 2009 Nanotechnology Institute
Making Nanostructures: Nanomanufacturing

"Top down" versus "bottom up" methods

- Lithography
- Deposition
- Etching
- Machining

- Chemical
- Self-Assembly
As you view the following images you should consider the question:

What drives and governs self assembly?
Tobacco Mosaic Virus

wisc.edu

nih.gov
Gecko feet
Diatoms

priweb.org

sinancanan.net
Abalone
The Cell and Its Hierarchy

diagram showing cell components such as microtubules, mitochondrion, centriole, vesicle, cytosol, rough endoplasmic reticulum, ribosomes, Golgi complex, lysosome, flagellum, and plasma membrane.
Self assembly at all scales?

Whitesides et al. *Science* **295**, 2418 (2002);
What drives self assembly?

- **Static assembly** *(thermodynamic free energy minimum)* -- once formed it is stable
- **Dynamic assembly** *(kinetically formed, not necessarily thermodynamic minimum)* -- not necessarily stable

- **Forces of chemical bonding** *(4)*
  - covalent, ionic, van der Waals, hydrogen
- **Other forces** *(magnetic, electrostatic, fluidic, …)*
- **Polar/Nonpolar** *(hydrophobicity)*
- **Shape** *(configurational)*
- **Templates** *(guided self assembly)*
- **Kinetic conditions** *(e.g., diffusion limited)*


Excerpt from Letter of Benjamin Franklin to William Brownrigg (Nov. 7, 1773)

...At length being at Clapham, where there is, on the Common, a large Pond ... I fetched out a Cruet of Oil, and dropt a little of it on the Water. I saw it spread itself with surprising Swiftness upon the Surface ... the Oil tho' not more than a Tea Spoonful ... which spread amazingly, and extended itself gradually till it reached the Lee Side, making all that Quarter of the Pond, perhaps half an Acre, as smooth as a Looking Glass....
Langmuir Film

of an amphiphilic molecule
Langmuir-Blodgett Film

Must control movable barrier to keep constant pressure

Multiple dips - multiple layers
SAM: Self Assembled Monolayer

alkanethiol on gold (Au)  \( \text{HS(\text{CH}_2)_nX} \)  where X is the end group of the chain 
−\text{CH}_3, −\text{OH}, or −\text{COOH}

Longer alkanethiol molecules have greater thermodynamic stability

SAM: Self Assembled Monolayer

- Chemisorbed molecules
- Stabilized by intermolecular van der Waals interaction
There are now many configurations and uses of SAMs.

Nanoparticle Monolayer Formed at a Liquid-Air Interface
Nanoparticle Monolayer Formation

Requirements:
- rapid evaporation
- excess dodecane present
- attractive interaction to liquid-air interface and between particles
SELF ASSEMBLY with DIBLOCK COPOLYMERS

Block “A”
PMMA

~10 nm

Block “B”
PS

Scale set by molecular size

Ordered Phases

10% A

30% A

50% A

70% A

90% A
CORE CONCEPT FOR NANOFABRICATION

Deposition Template
(physical or electrochemical)

Etching Mask

Nanoporous Membrane

Remove polymer block within cylinders (expose and develop)

Versatile, self-assembling, nanoscale lithographic system
TEMPLATE CHARACTERIZATION

PS/PMMA
MW = 42,000

SEM

Array Period = 24 nm
Pore Diameter = 14 nm

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Pore Diameter = 14 nm
Improving Order: Guided Assembly in a Trench: Graphioepitaxy

side view

assemble here

top view

UMass-Seagate
Nanomagnets in a Self-Assembled Polymer Mask

nanoporous template

1x10^{12} magnets/in^2

Data Storage...
...and More
Metal Nanorings

Ferromagnetic cobalt rings as small as 15 nm OD
Kinetic Self-Assembly - by Breath Figures

More Fabrication by Breath Figures

a, Breath-figure pattern obtained with pure polystyrene. b, Optical and c, confocal fluorescence microscope images of different areas of a sample obtained from solvent-casting a polystyrene film from chloroform with CdSe nanoparticles. Scale bars: 16 mum. The inset in c shows a fluorescence intensity scan along the line indicated.

Anodized Aluminum Oxide Templates

Anodization Acid Bath (oxalic, sulfuric, or phosphoric acid)

Nanoporous aluminum oxide (AAO)

counter electrode

~ 40 V

I

e.g., • Keller, et al., J. Electrochem. Soc. 100, 411 (1953)
Proposed AAO Growth Mechanism

- Density mismatch between Al and Al$_2$O$_3$
- Some Al$^{3+}$ goes to solution
- Mechanical stress yields pore growth in uniform hexagonal array

Pore diameters of ~10-400 nm possible by choice of anodization conditions

Figure adapted from Jessensky, Müller, & Gösele, Appl. Phys. Lett. 72, 1173 (1998)
Improving AAO Order at Surface

SiC stamp

Aluminum

→ anodize

Ni in Anodized Aluminum Oxide Template

Large Scale Self-Assembly (Geological)

Giant's Causeway
(Northern Ireland)

Volcanic basalt cooled rapidly to form these (mostly) hexagonally shaped columns
Microfluidic Assembly

*Alien Technology*

Application: RFID

Parts, having unique shape, are delivered via fluid flow to mating pockets on an assembly substrate.

Nanoscale Phase Separation

IBM "air gap" technology

Introducing nanoscale air pockets into the insulating material separating wires on a computer chip -- lowers the capacitance.
Molecular Recognition
("lock and key" bonding)

hydrogen bonding

thymine (T) ⇔ adenine (A)

guanine (G) ⇔ cytosine (C)

biotin-avidin pair (site-specific binding)
Designer DNA molecules can be synthesized chemically, and allowed to assemble into a specific configuration of lowest energy.
Programmed DNA Folding to Make "DNA Origami"

Additional examples to amplify concepts

- balls in a box
- magnets
- crystallization

Forces (non-directional or directional), shape, thermal agitation
Nanoscale self assembly
- coffee stain
- nanoparticle assembly by droplet
- others