Self-assembly and Nanotechnology 10.524

Lecture 2. Fundamentals and Theories of Self-Assembly

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& UML CHN/NCOE Nanomanufacturing Center)

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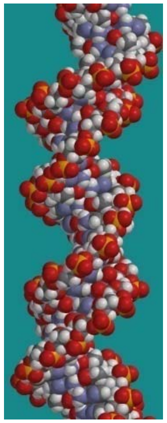
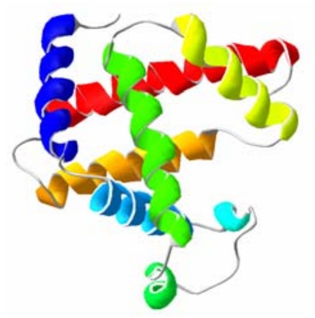
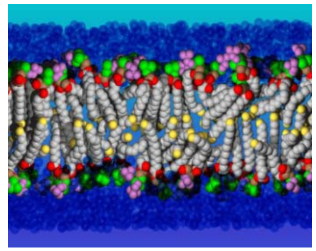
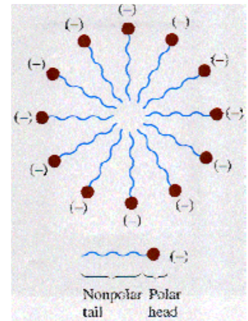
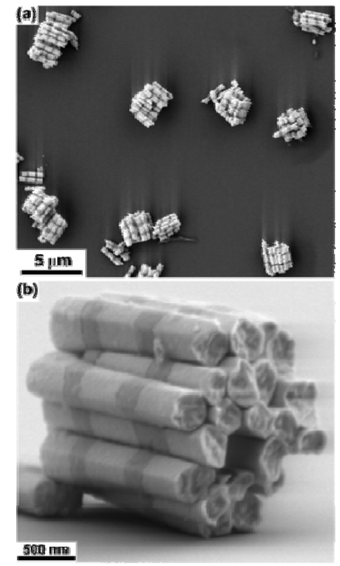
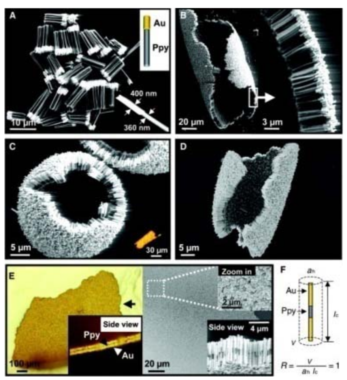


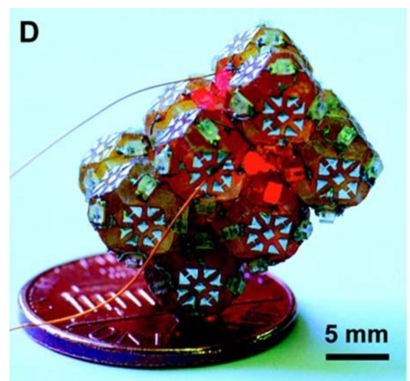












- Why self-assembly can happen?
- What are common features?

Forces, energy, entropy

Fundamentals and Theories of Self-Assembly

Various forces and examples

- Covalent bond (chemical bonding
- Van der Waals
- Electrostatic
- Hydrogen Bonding
- Hydrophobic
- Hydration
- ●●●

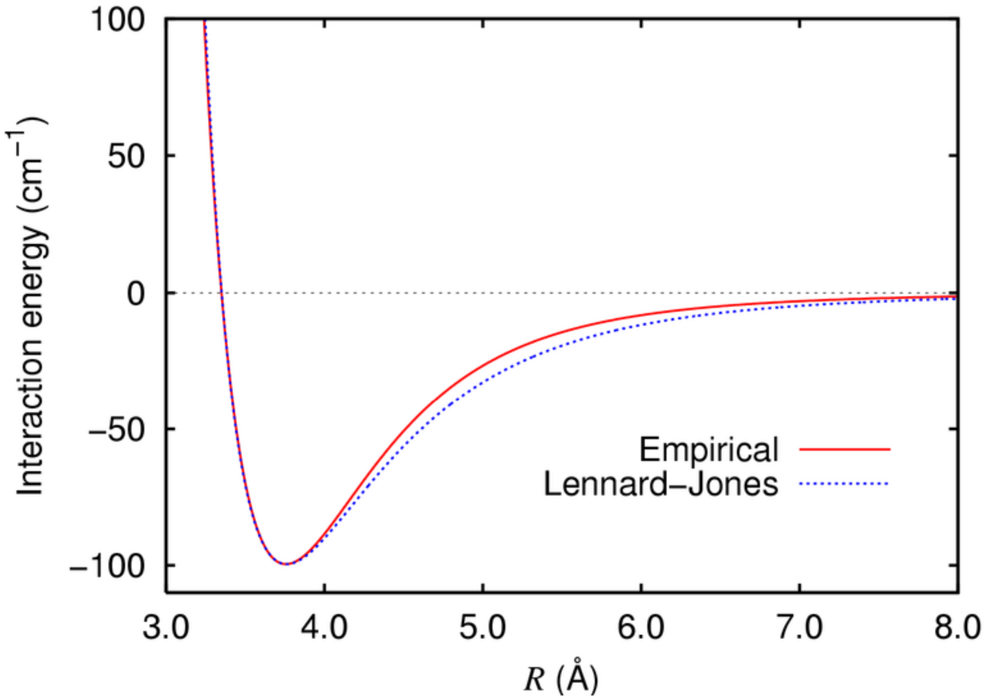
- Magnetic force
- Electrical force
- Gravity
- ●●●

Van der Waals' forces

Lennard-Jones potential

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where ε is the depth of the potential well and σ is the (finite) distance at which the potential is zero.



From Wikipedia

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Fundamentals and Theories of Self-Assembly

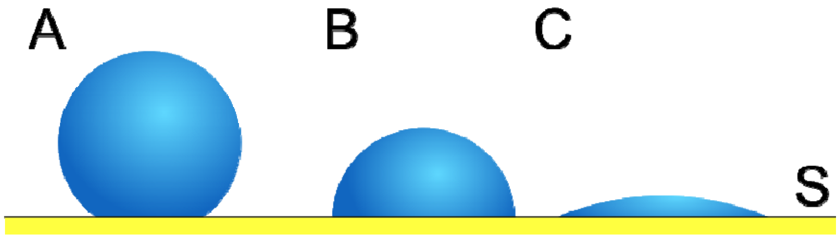
Hydrophobic force

Hydrophobic: Does not like water

Contact angle: > 90°

Hydrophilic: like water

Contact angle: < 90°

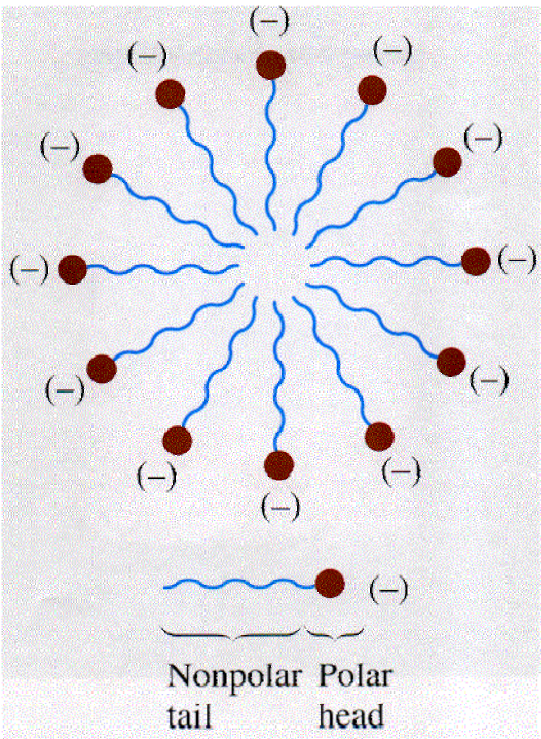


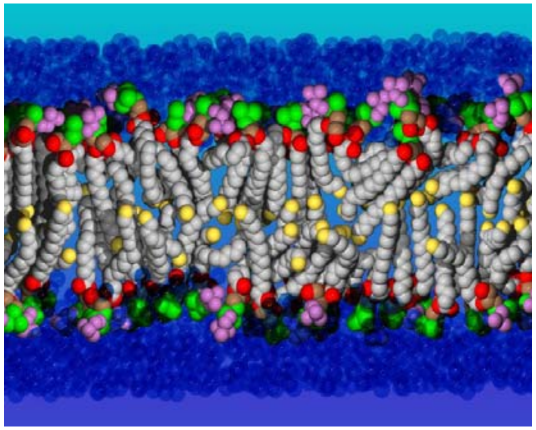
Wetting of different fluids

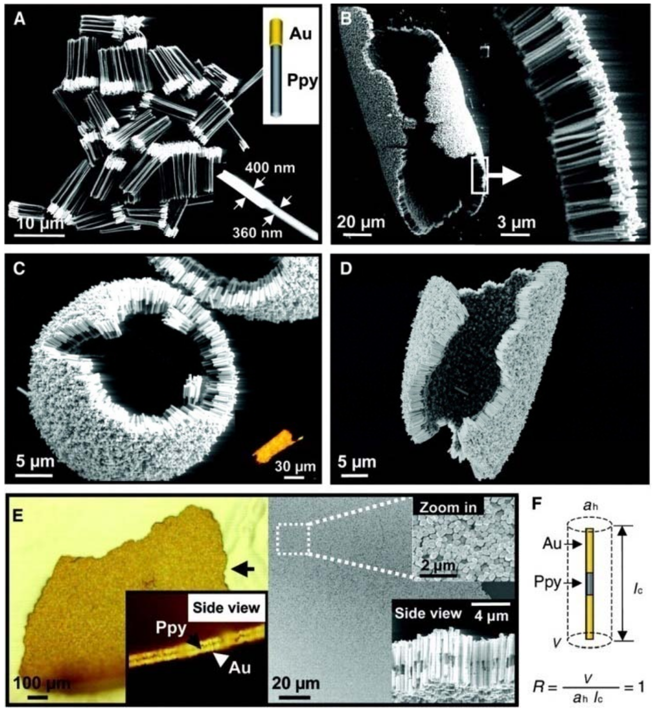
From Wikipedia

Fundamentals and Theories of Self-Assembly

Hydrophobic force: self-assembly examples







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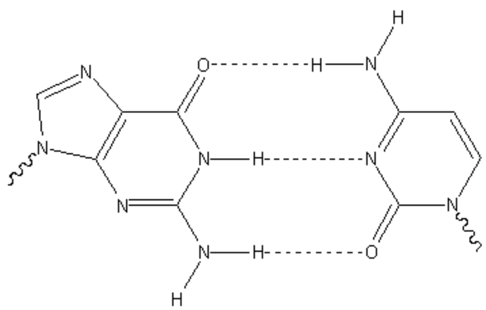
Fundamentals and Theories of Self-Assembly

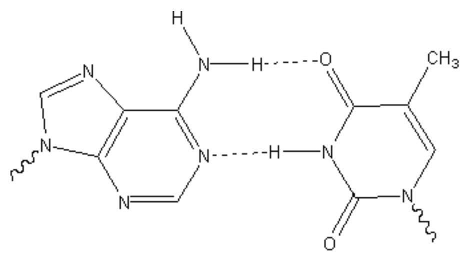
DNA self-assembly and Molecular Computing

Deoxyribonucleic acid (**DNA**) is a nucleic acid that contains the genetic instructions for the development and function of living organisms.

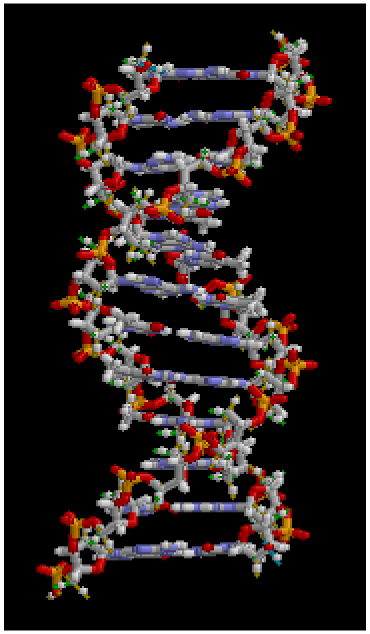
The DNA double helix is held together by hydrogen bonds between the bases attached to the two strands. The four bases found in DNA are adenine (abbreviated A), cytosine (C), guanine (G) and thymine (T).



Guanine Cytosine



Adenine Thymine

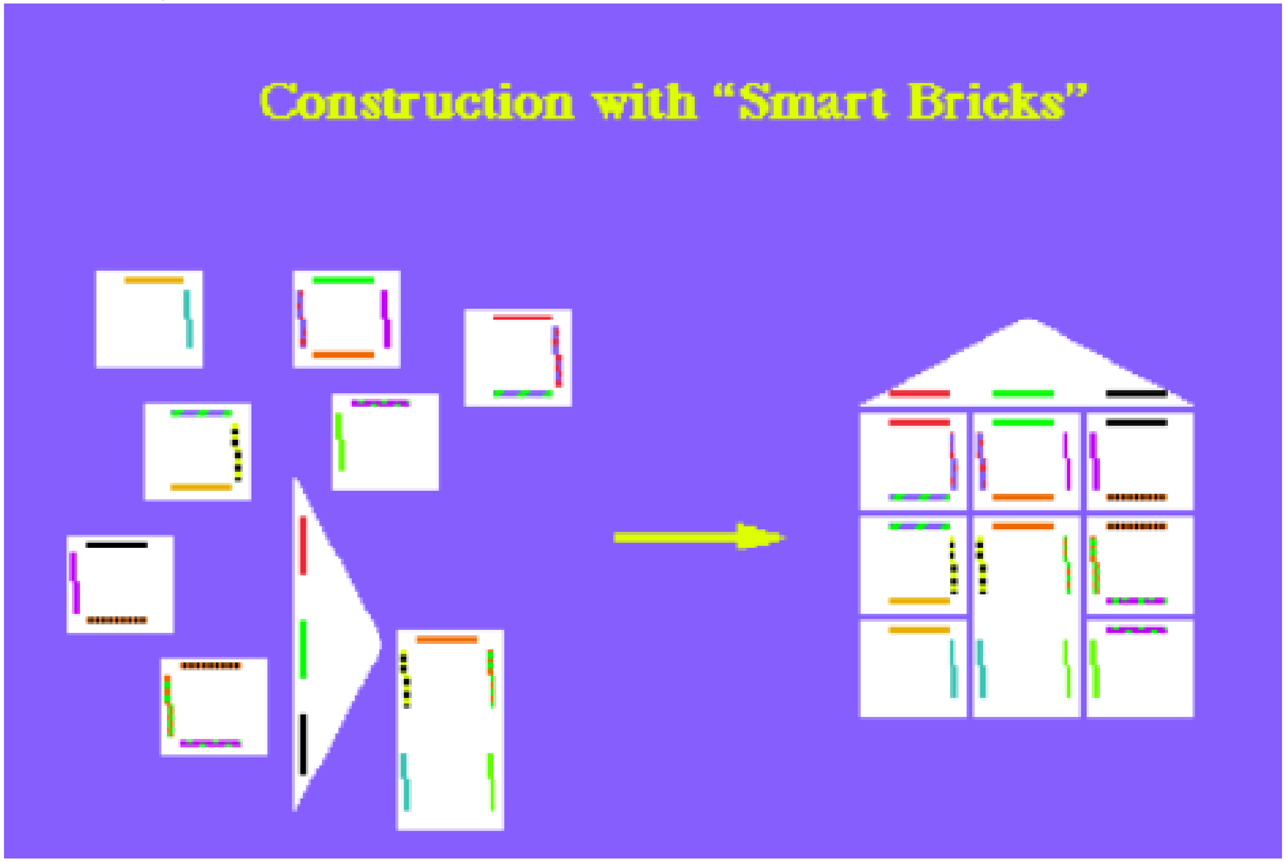


DNA self-assembly is the most advanced and versatile system known for programmable construction of patterned systems on the molecular scale

Reif, Duke Univ.

Fundamentals and Theories of Self-Assembly

DNA self-assembly and Molecular Computing



Reif, Duke Univ.

Fundamentals and Theories of Self-Assembly

DNA self-assembly and Molecular Computing

An experimental demonstration of an XOR tiling computation based on TAO tiles is reported in [Mao, LaBean, Reif, and Seeman, 00].

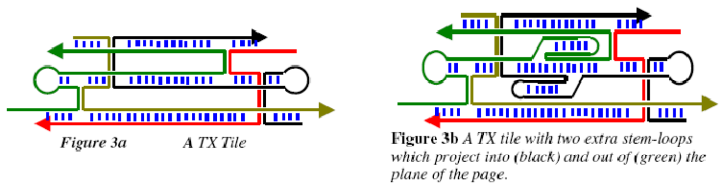
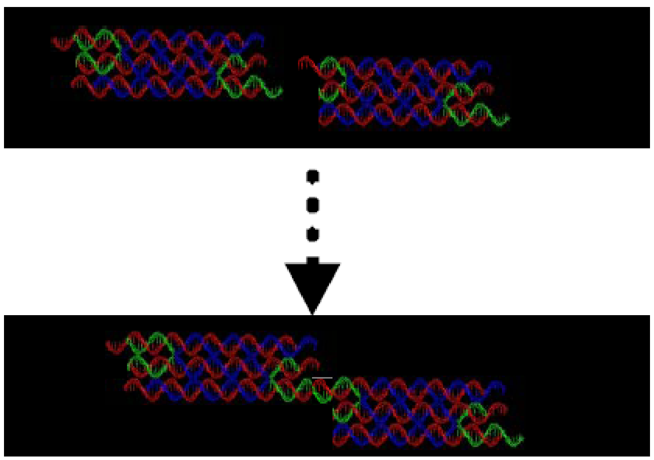
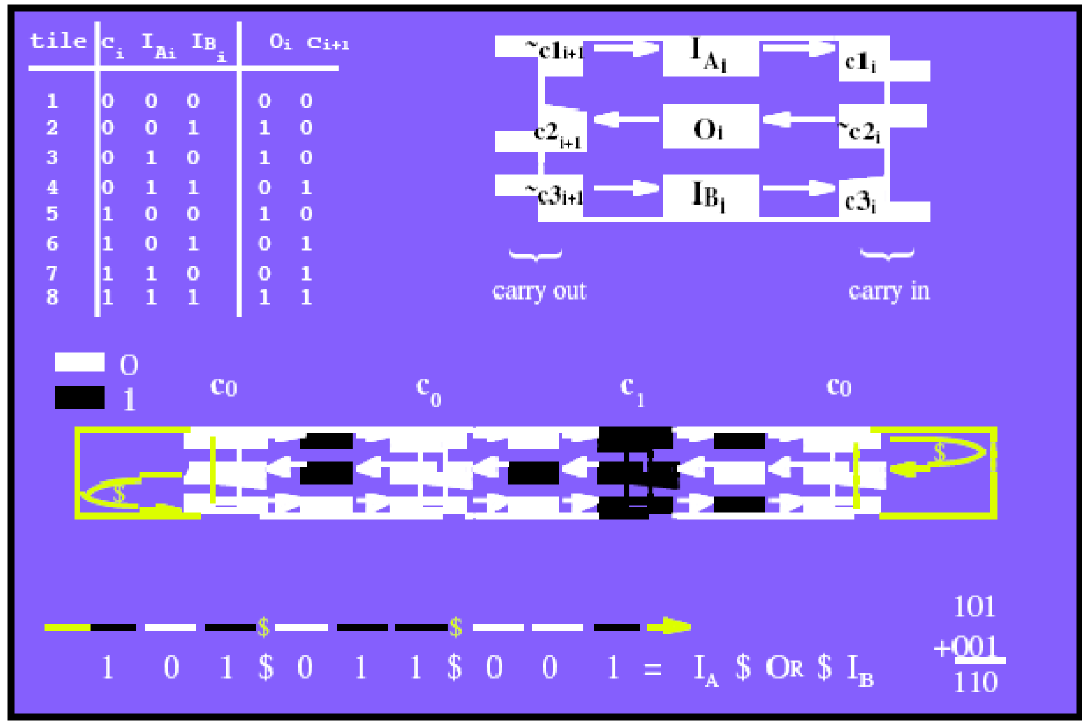


Fig. 3. (a) A triple-crossover tile and (b) a triple-crossover tile that has two extra stem-loops that project into (black) and out of (green) the plane of the page.



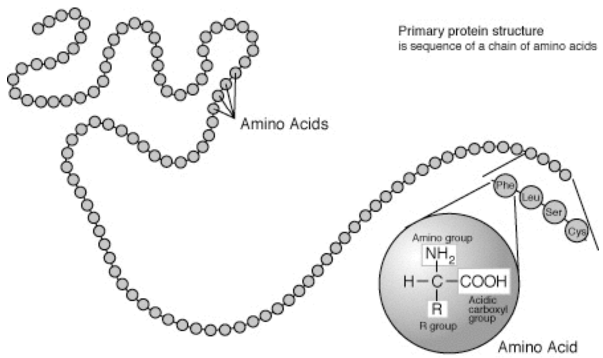
The binding of DNA tile pad pairs



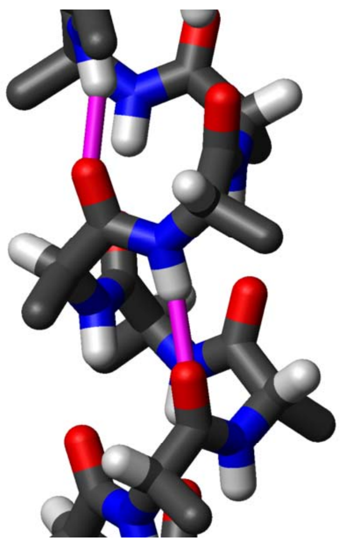
Reif, Duke Univ.

Protein structures

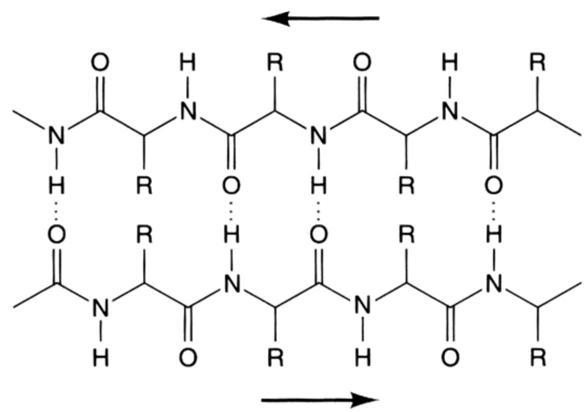
Primary structure: amino acid sequence



Secondary structure: regularly repeating local structures stabilized by hydrogen bonds



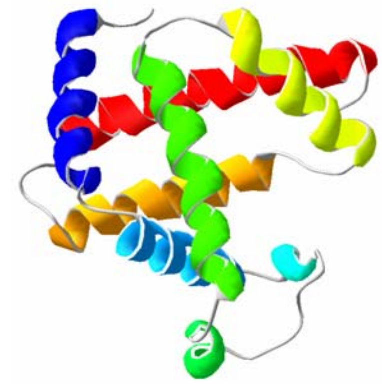
alpha helix (α-helix)



β sheet (also β-pleated sheet)

From Wikipedia

Protein structures



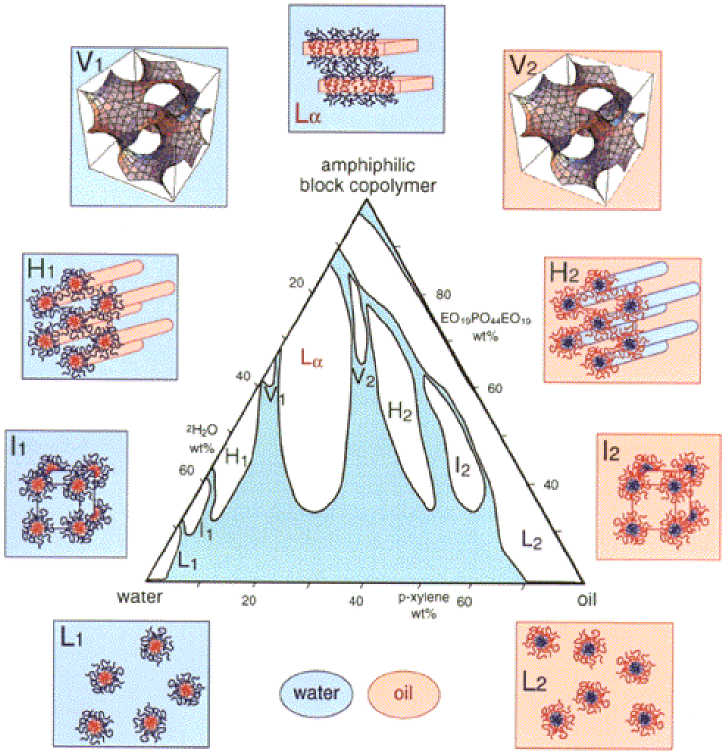
Tertiary structure: the overall shape of a single protein molecule; the spatial relationship of the secondary structures to one another.

Tertiary structure is generally stabilized by nonlocal interactions, most commonly the formation of a hydrophobic core, but also through salt bridges, hydrogen bonds, disulfide bonds, and even post-translational modifications.

Quaternary structure: the shape or structure that results from the interaction of more than one protein molecule, usually called *protein subunits* in this context, which function as part of the larger assembly or protein complex.

From Wikipedia

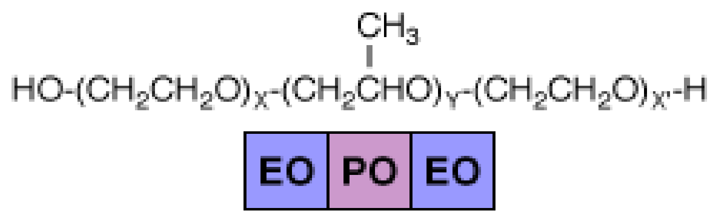
Case Study: Measurement of Intermolecular Forces/Interactions



Ordered nanostructures of block copolymers

Alexandridis, Olsson, Lindman, *Langmuir* **1998**, *14*, 2627-2638

Pluronics®, or Poloxamers, are poly(ethylene oxide) b-poly(propylene oxide)-b-poly(ethylene oxide) block copolymers which consist of two hydrophilic PEO blocks and one hydrophobic PPO block.



PEO-PPO-PEO block copolymers can form a variety of self-assembled nanostructures in water (selective solvent for PEO).

Spherical micelles in solution; micellar cubic, hexagonal, lamellar, bicontinuous lyotropic liquid crystalline phases, etc.

Pluronics® find numerous applications in coatings and personal care formulations, and also in the areas of biomaterials, drug delivery and drug formulations.

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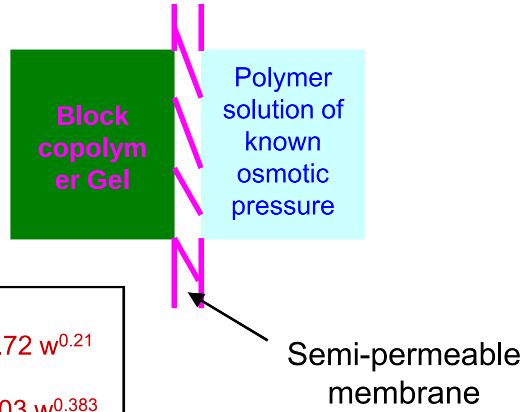
Intermolecular Forces/Interactions in Block Copolymer Assemblies

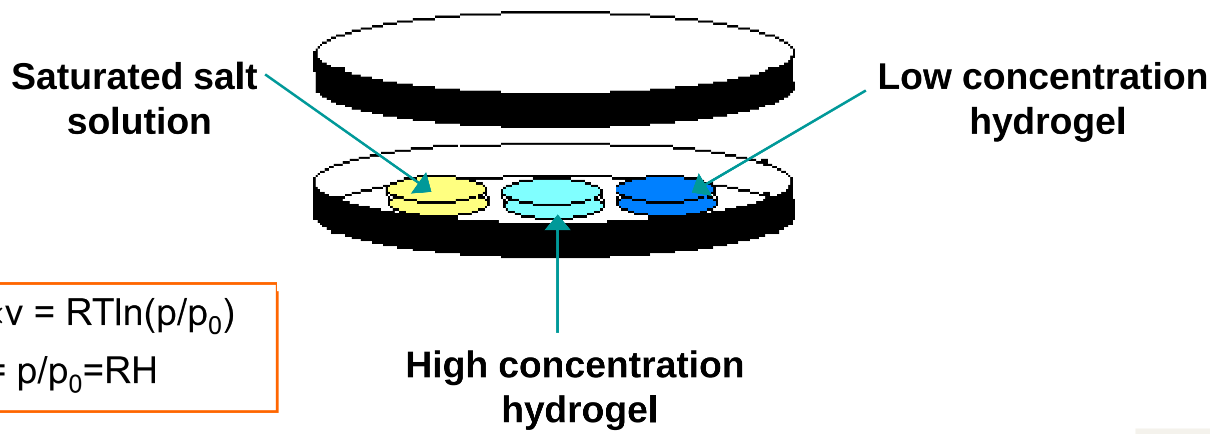
Osmotic stress (OS) measurements

I. Equilibration with Polymer solutions



PEG2000:
$\log [\Pi_{PEG}] = 1.61 + 2.72\, w^{0.21}$
Dextran T500:
$\log [\Pi_{DEX}] = 2.75 + 1.03\, w^{0.383}$

II. Equilibration with saturated salt solutions



$\mu = -\pi \times v = RT\ln(p/p_0)$

$a = p/p_0 = RH$

Parsegian, V. A.; et al. *Methods Enzymol.* **1986**, *127*, 400-416.

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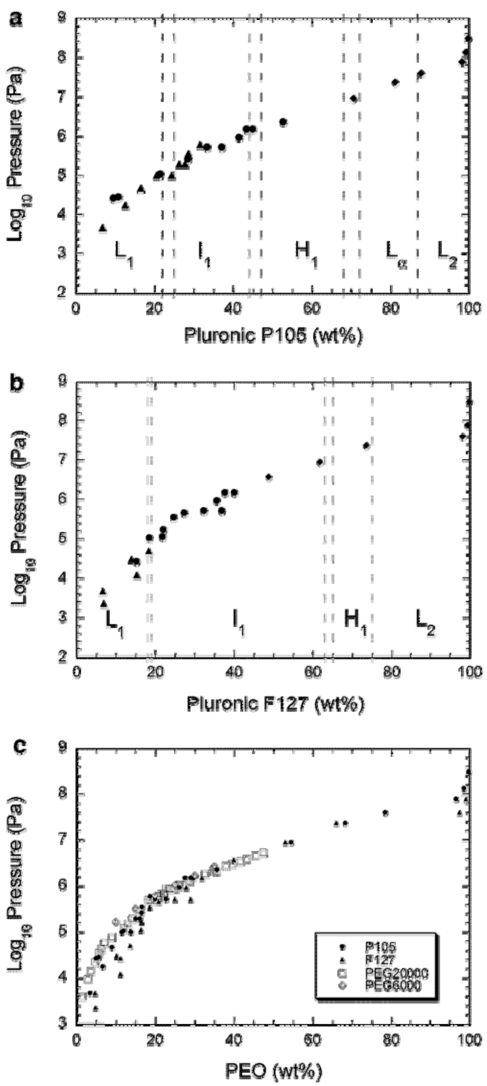
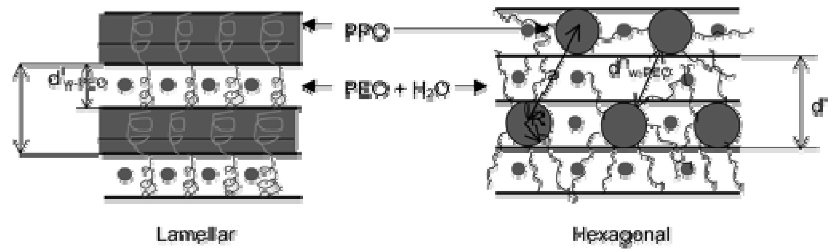
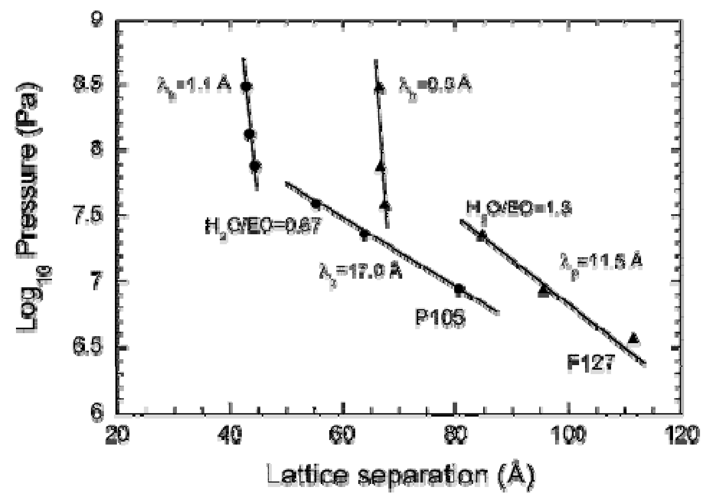
Intermolecular Forces/Interactions in Block Copolymer Assemblies





SAXS
SANS



- Osmotic pressure is an exponential function of block copolymer concentration. PEO-water interactions contribute more to the osmotic pressure of Pluronic-water systems.
- Different interactions have been observed at different concentration range of Pluronic-water systems.
- Two different decay lengths are observed at force vs. distance curve; one is comparable to PEO coil, another similar to "hydration force".

Gu and Alexandridis. *Macromolecules* **2004**, *37*, 912-924.

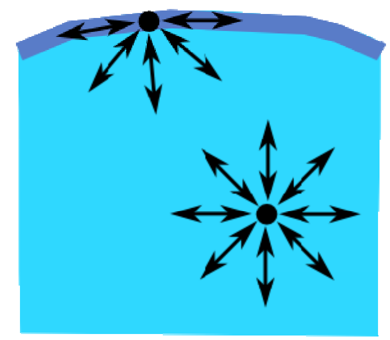
Surface Tension-Powered Self-Assembly

Surface Tension-Powered Self-Assembly

What's surface tension??

In physics, **surface tension** is an effect within the surface layer of a liquid that causes that layer to behave as an elastic sheet

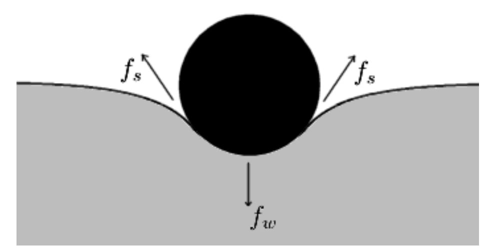
Surface tension is caused by the attraction between the molecules of the liquid by various intermolecular forces



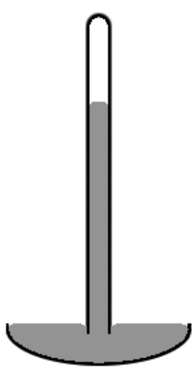
Forces on a molecule of liquid

Liquid in a vertical tube

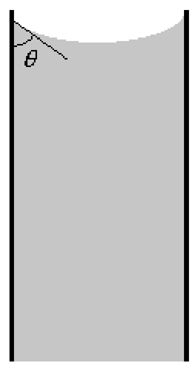
$$h = \frac{2\gamma_{\mathrm{la}} \cos\theta}{\rho g r}$$



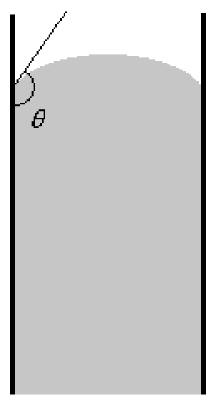
A needle floating on the surface of water



Hg barometer



Concave meniscus

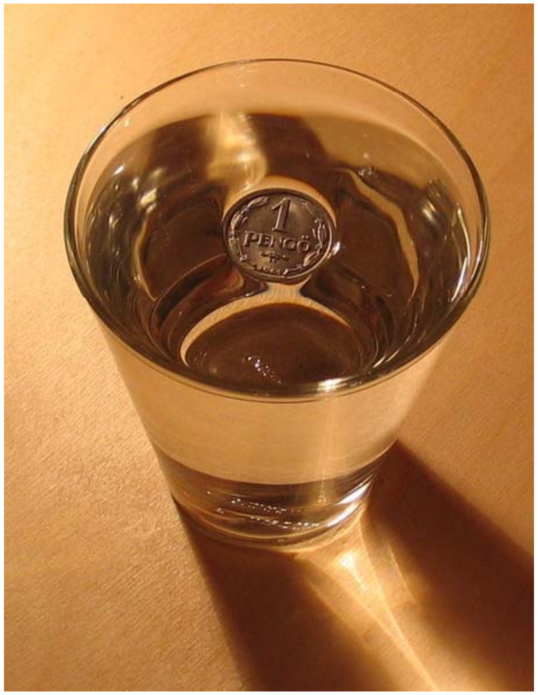


Convex meniscus

From Wikipedia

Surface Tension-Powered Self-Assembly

Surface tension in everyday life



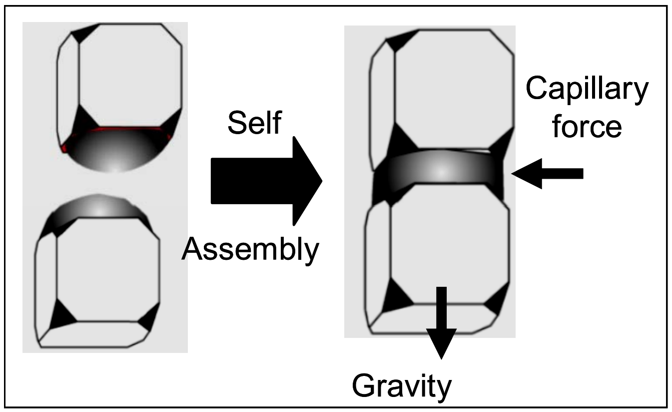
From Wikipedia

Surface Tension-Powered Self-assembly

Surface tension is dominating at micro and nano-scale

Why surface tension force?

- Surface tension forces are very strong on the nanoscale
- Roughness not a problem: Large scale integration possible



Scaling law

$$\frac{SurfaceTensionBasedForce}{Gravity(volume)} \approx \frac{r}{r^3} = \frac{1}{r^2}$$

e.g. for a 50 nm cube of copper coated with solder faces,

Solder (Sn/Pb): 542 dynes/cm
(H_2O: 72 dynes/cm at 25°C)

$$F\ (capillary) = 2\pi r \gamma \ \approx 1\text{x}10^{-7}\ \text{N}$$

$$F(gravity) = mg = Vdg \approx 2 \times 10^{-17}\ \text{N}$$

$$F\ (kT) \ \approx 1\text{x}10^{-13}\ \text{N}$$ (Thermal force)

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Surface Tension-Powered Self-Assembly

Two-dimensional geometry for surface tension powered rotation.

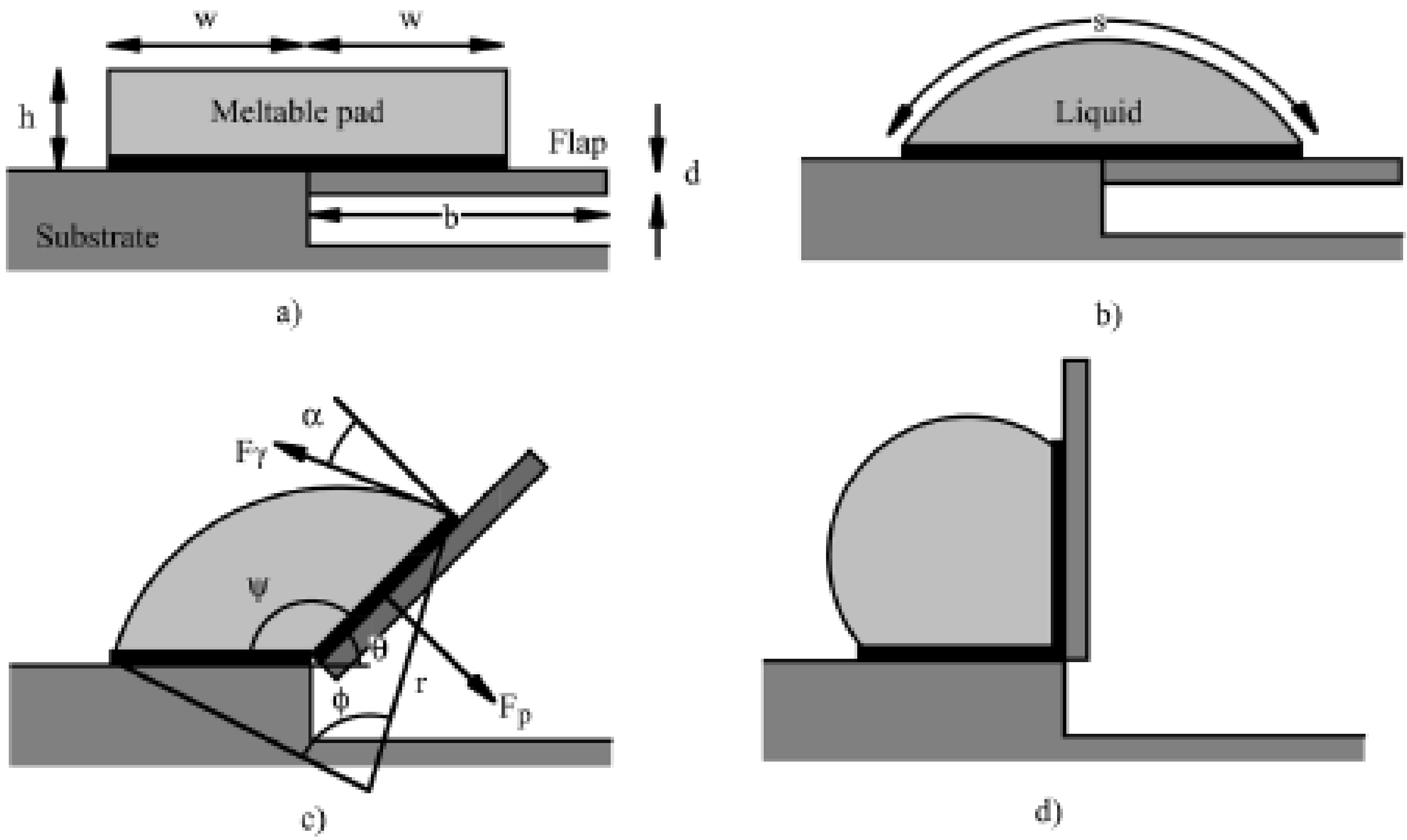
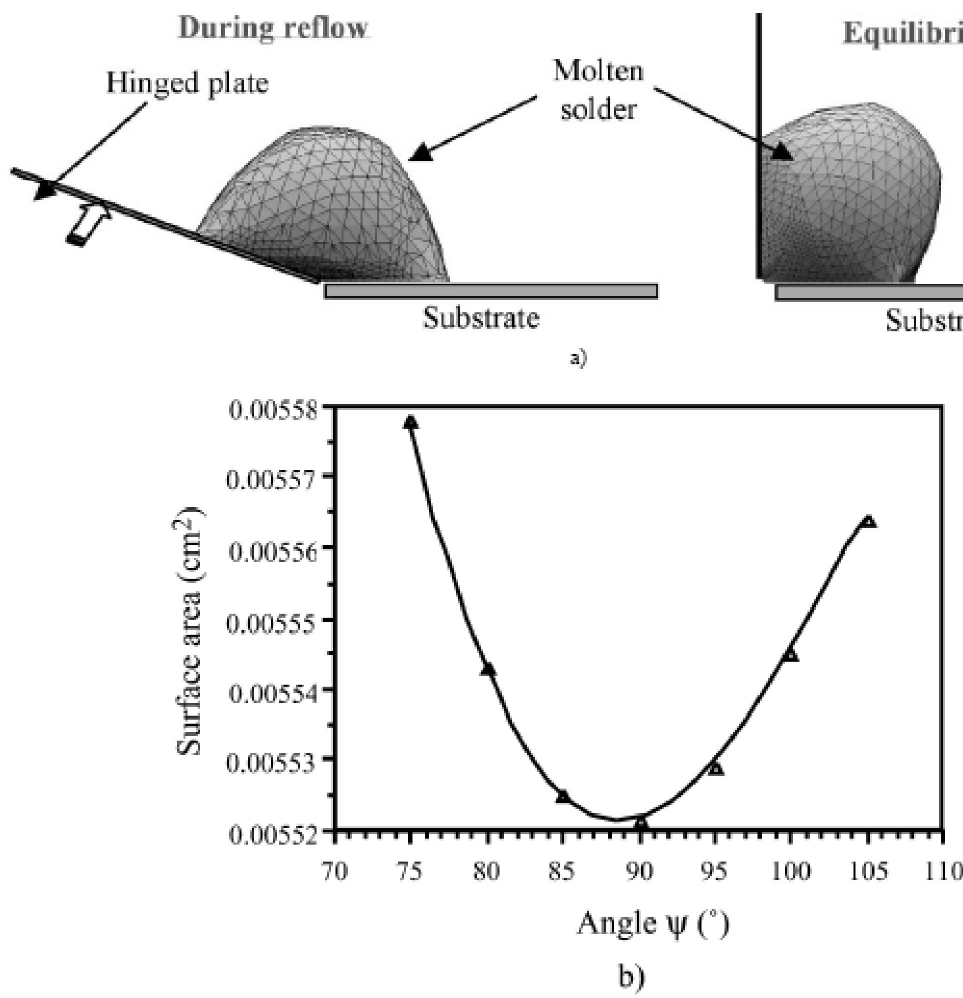


Fig. 3. Two-dimensional geometry for surface tension powered rotation.

Syms et al., 2003

Surface Tension-Powered Self-Assembly



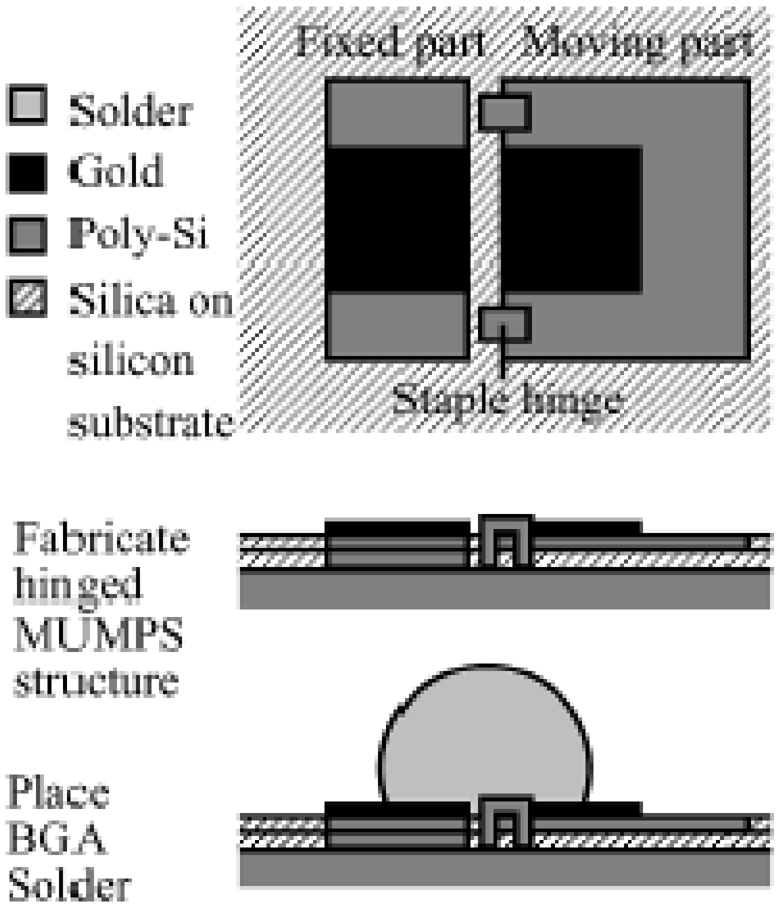
Syms et al., 2003

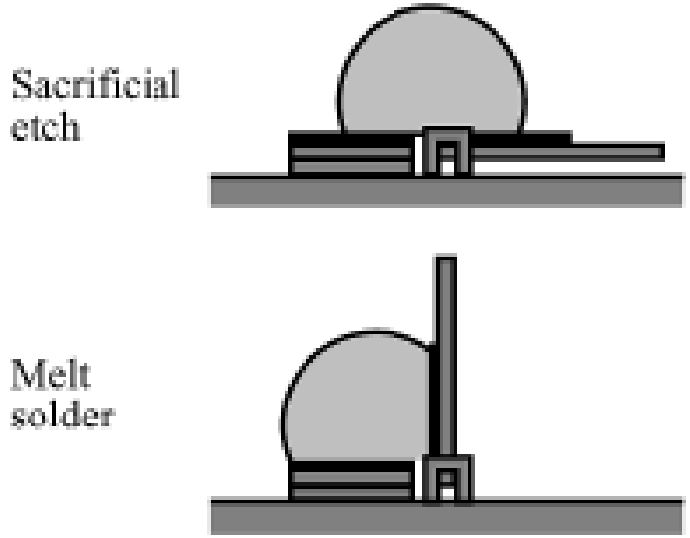
a) FE simulation of surface tension powered rotation;
b) variation of surface energy with angle,as predicted by the FE method

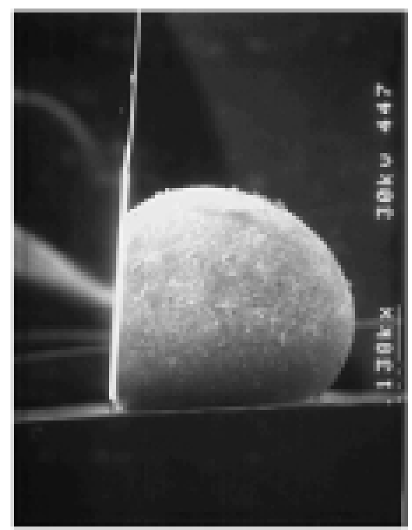
Self-assembly and Nanotechnology

Surface Tension-Powered Self-Assembly

Example I



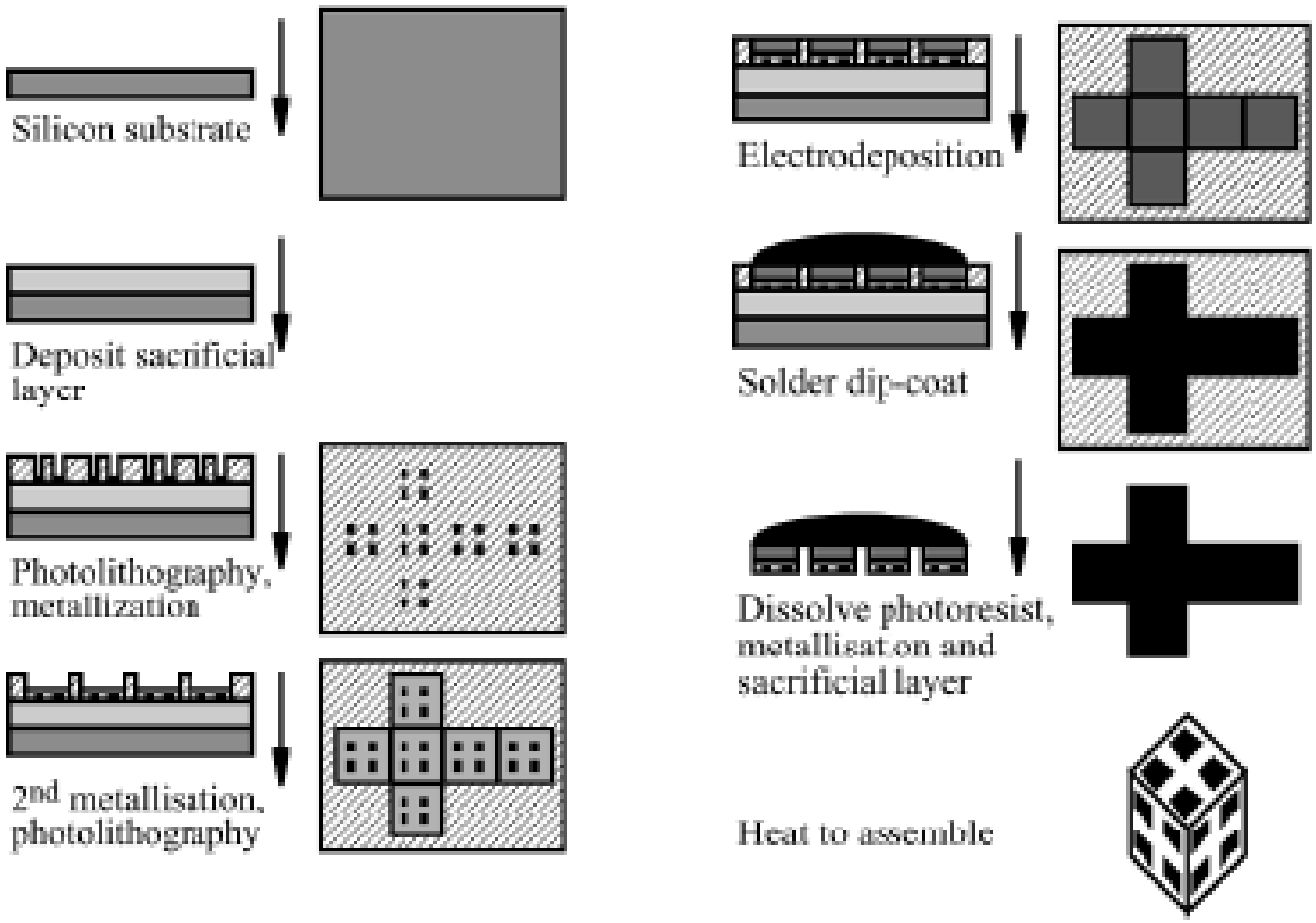




Syms et al., 2003

Surface Tension-Powered Self-Assembly

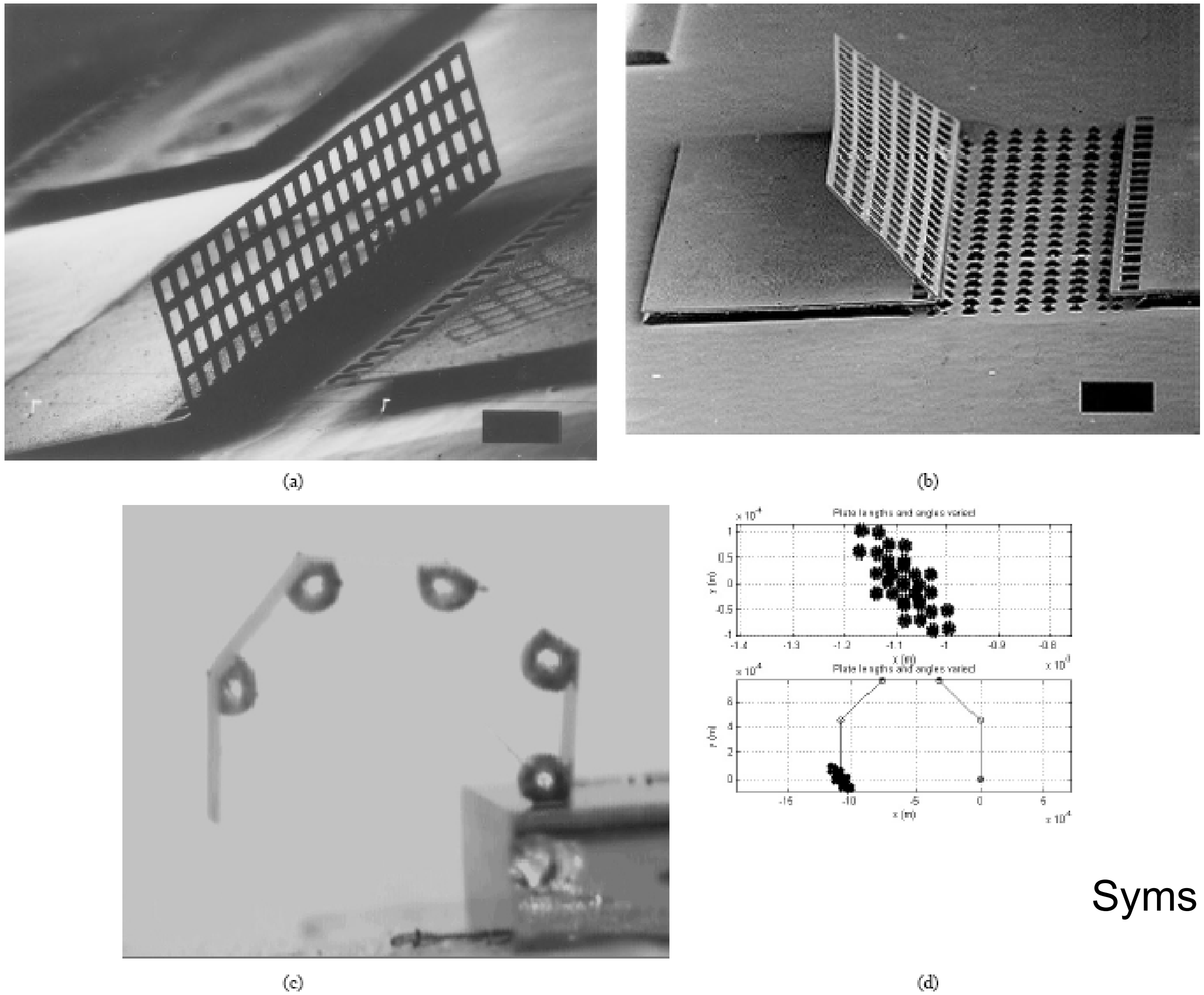
Example II



Syms et al., 2003

Surface Tension-Powered Self-Assembly

Some Examples



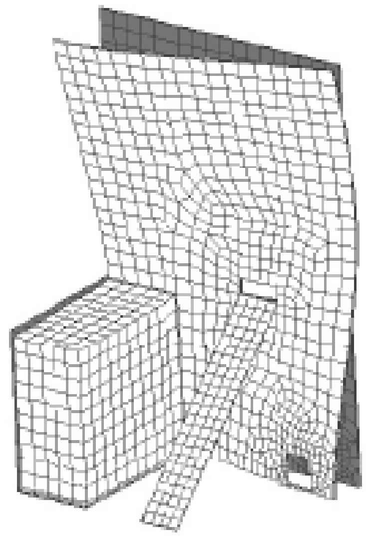
Syms et al., 2003

a) 90 rotation and b) over-rotation in hingelessstructures; c) 5-bar multiple link assembly, and d) simulation of assembly accuracy.

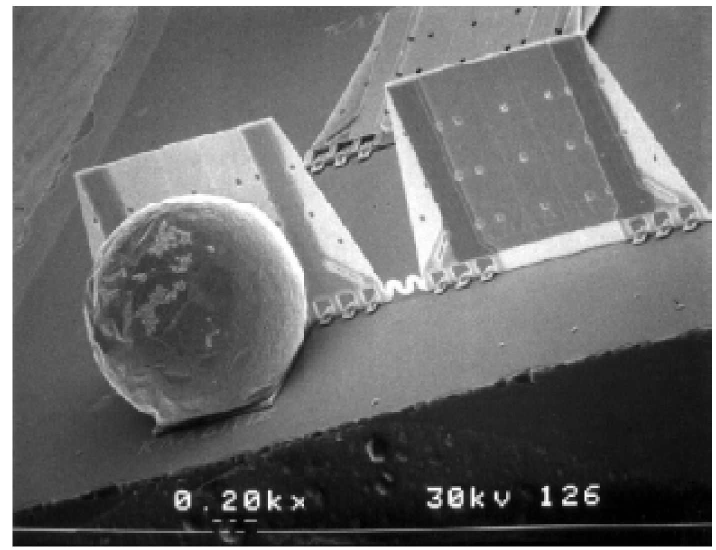
Surface Tension-Powered Self-Assembly

Some Examples

(a)



(b)



(c)

Syms et al., 2003

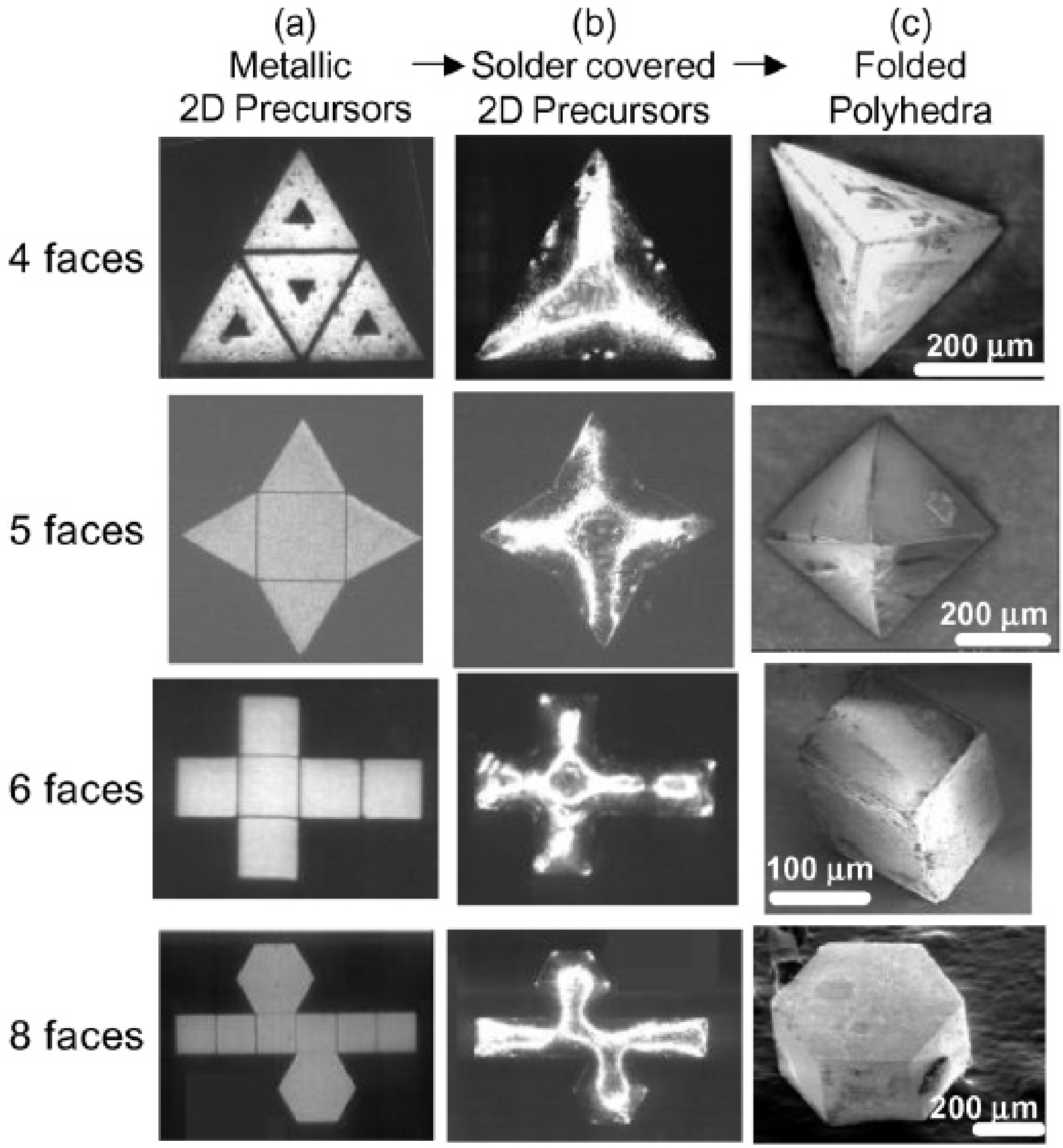
(a) Geometry and (b) predicted deformation of flap assembled using solder spheres; (c) mirrors assembled using solder self-assembly but attached via linkages.

Surface Tension-Powered Self-Assembly

Some Examples

(a) Metallic 2-D structures prior to folding; (b) 2-D precursors after dip-coating with solder; (c) completed polyhedra,ranging in size from 100 to 300 m per side

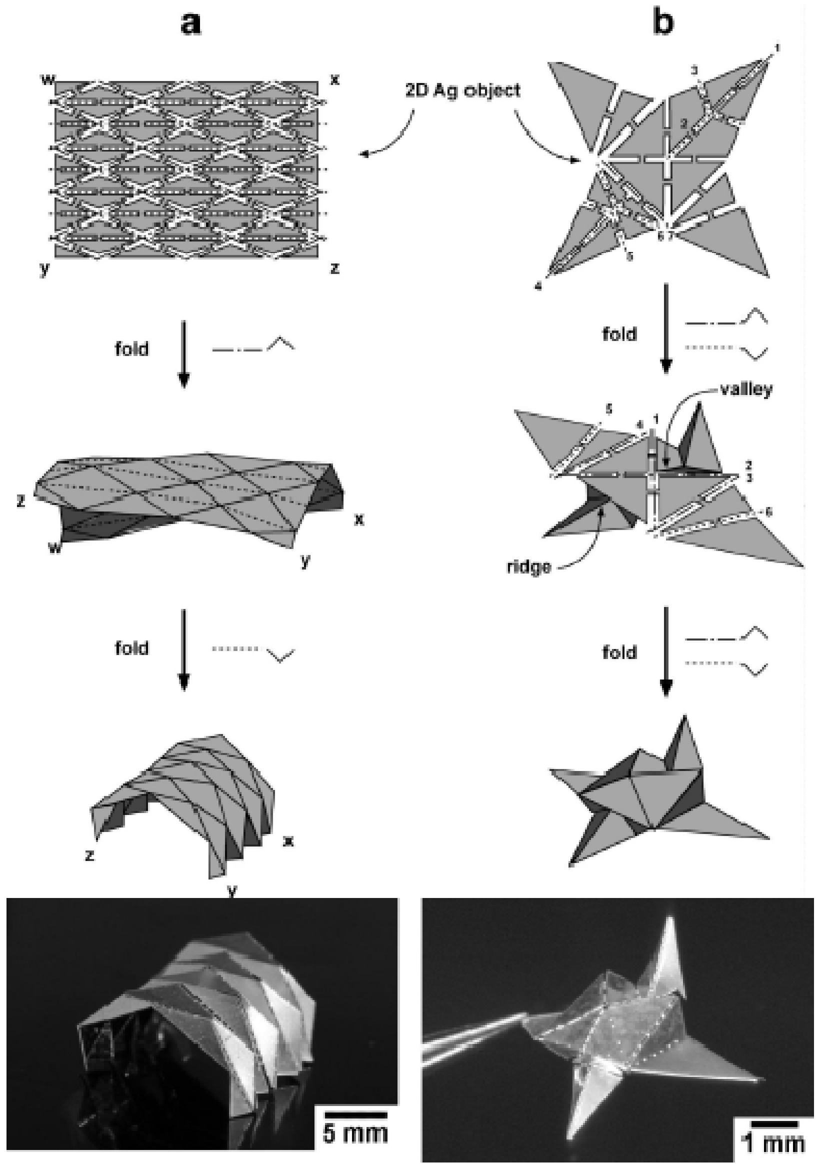
Syms et al., 2003



Surface Tension-Powered Self-Assembly

Some Examples

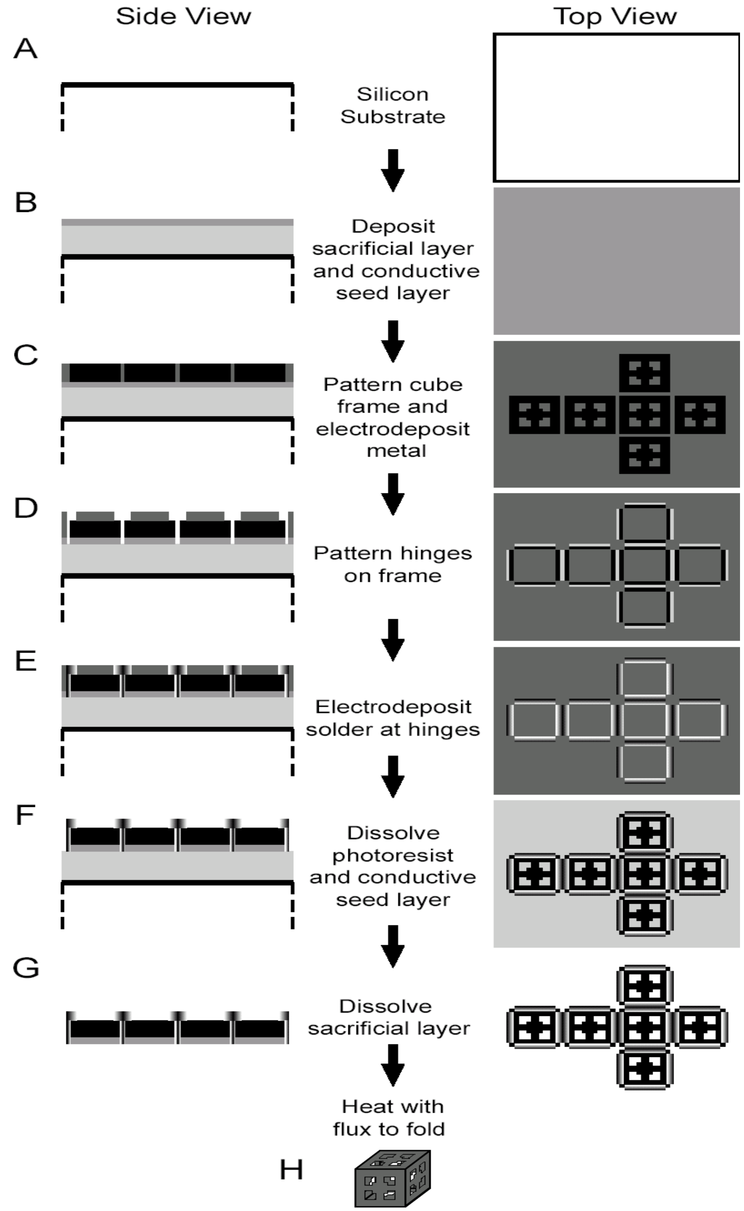
Syms et al., 2003



(a) Fold patterns and (b) completed structures for two micro-origami figures.

Case Study: Nano-liter Boxes for Encapsulation and Release

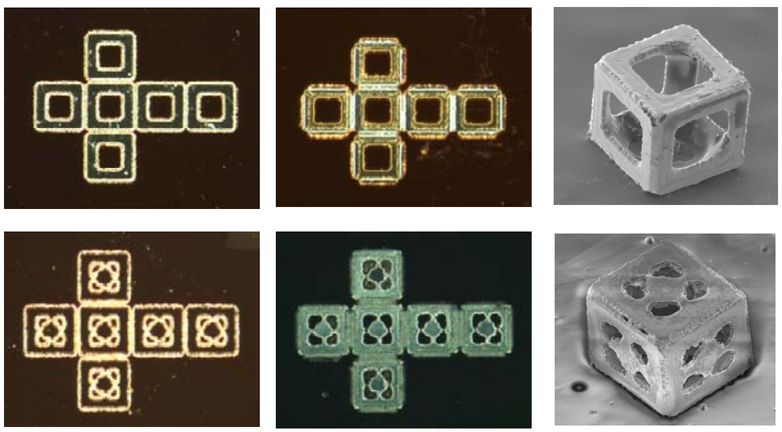
Fabrication and self-assembly

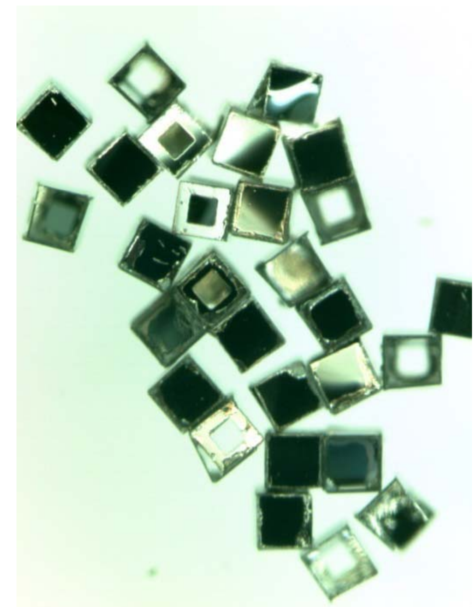


Gimi et al., Biomedical Microdevices, 2005

Case Study: Nano-liter Self-assembled Boxes

Fabrication and self-assembly

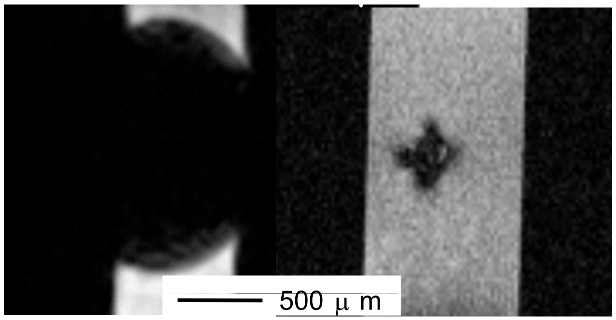


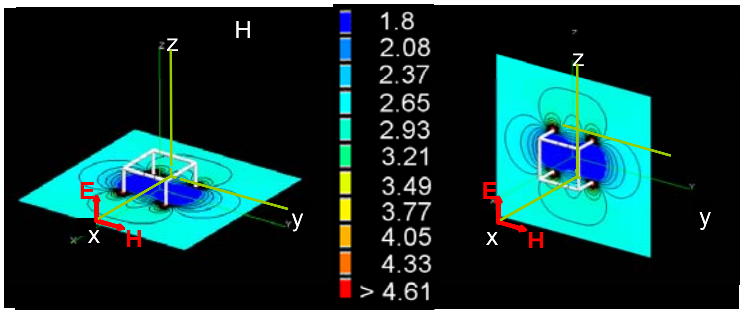


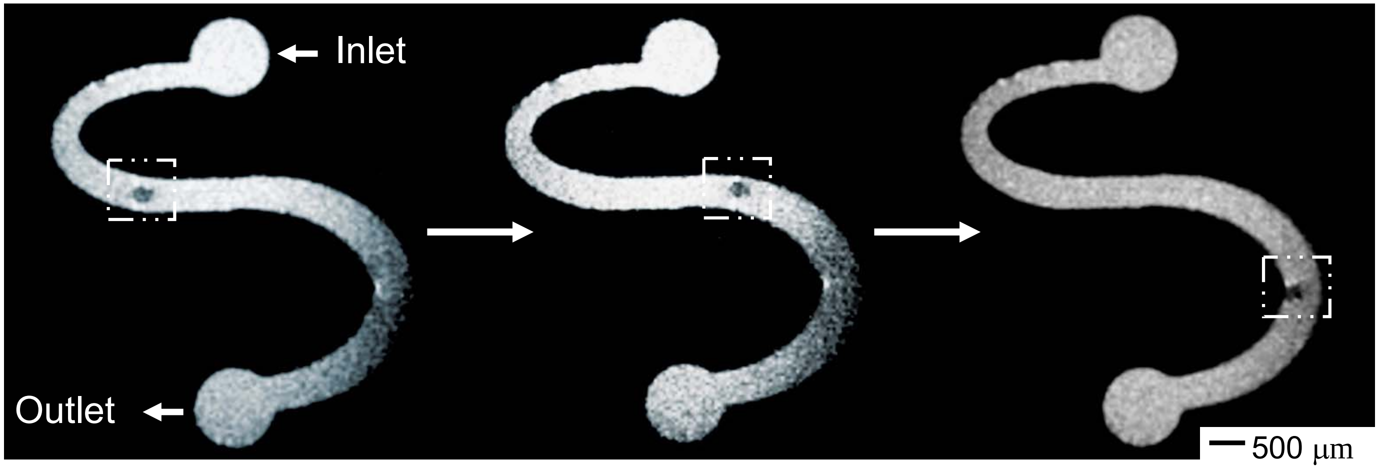
Gimi et al., Biomedical Microdevices, 2005

Case Study: Nano-liter Self-assembled Boxes

Magnetic Resonance Imaging (MRI) tracking



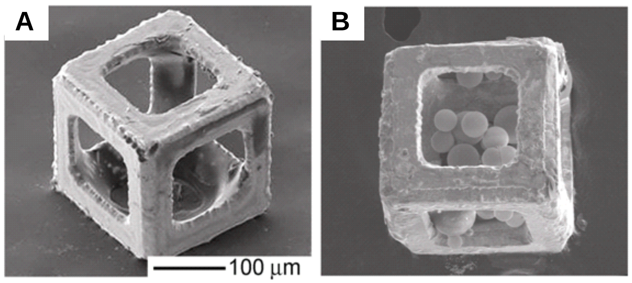


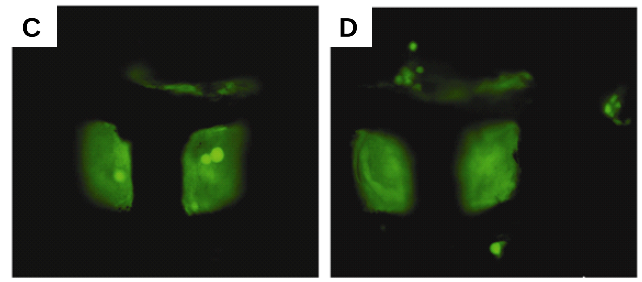


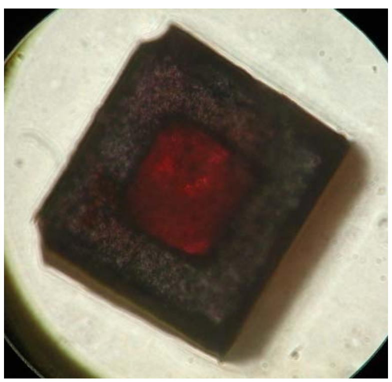
Gimi et al., Biomedical Microdevices, 2005

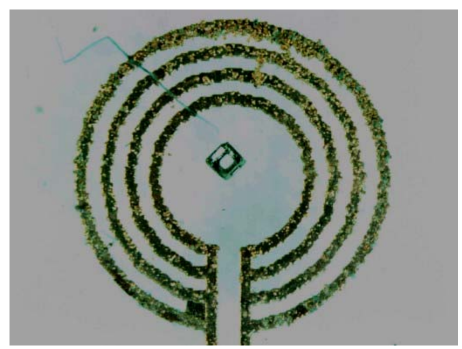
Case Study: Nano-liter Self-assembled Boxes

Particle and cell loading and controlled release





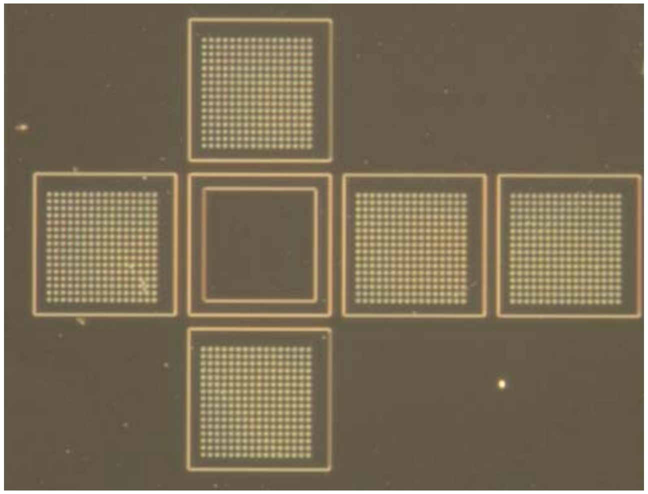


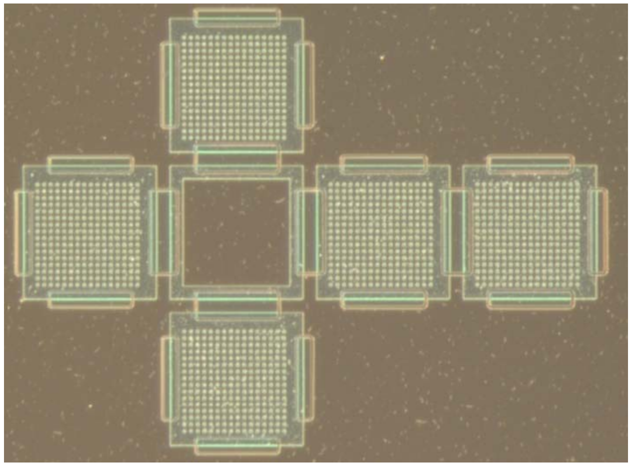


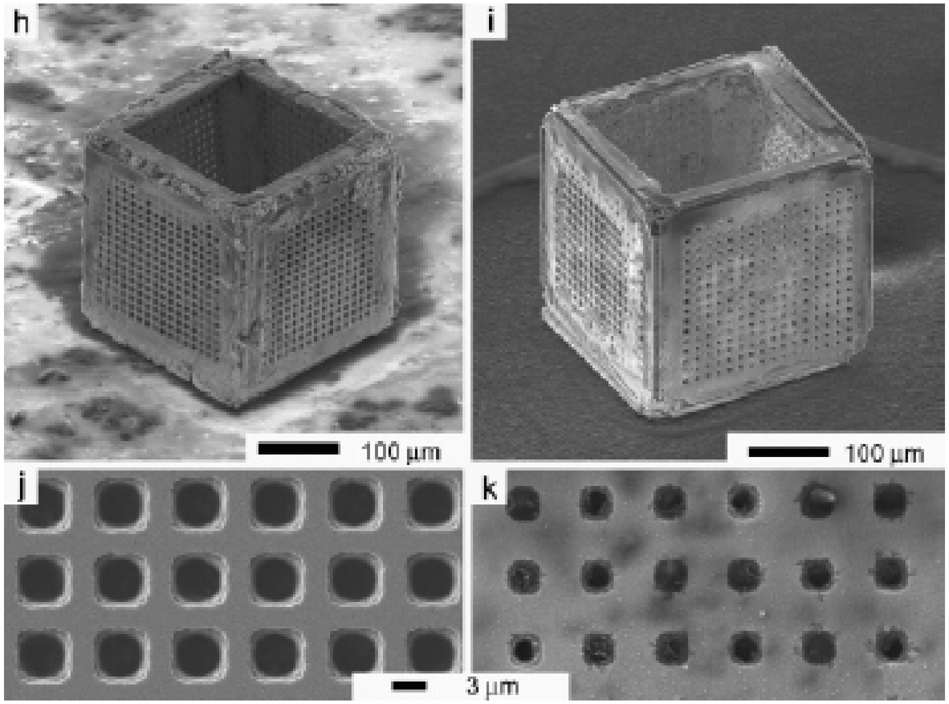
Gimi et al., Biomedical Microdevices, 2005

Case Study: Nano-liter Self-assembled Boxes

Controlling the porosity



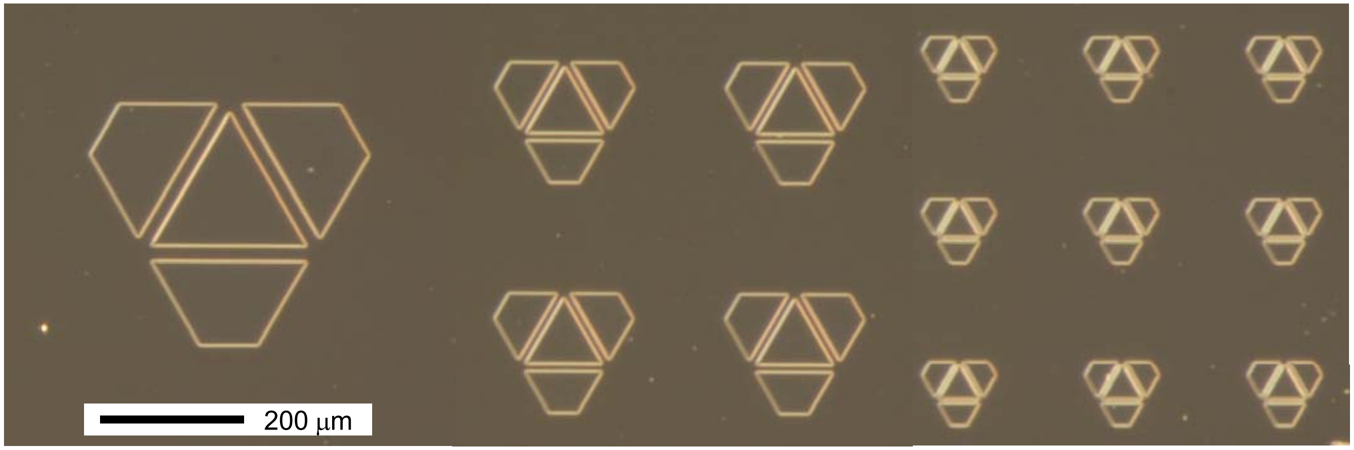


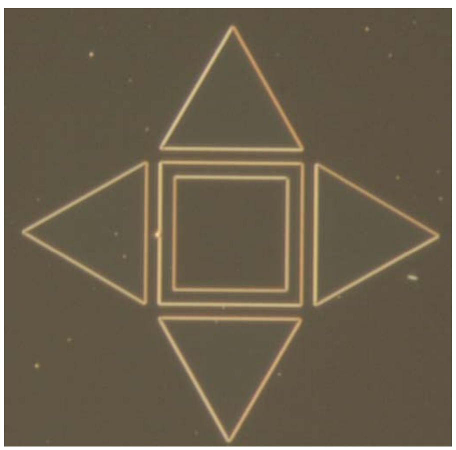


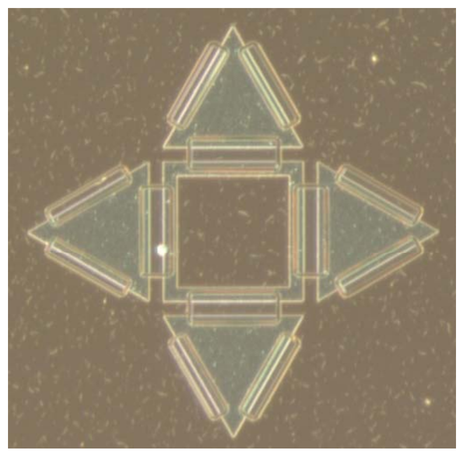
Leong et al., JACS, 2006

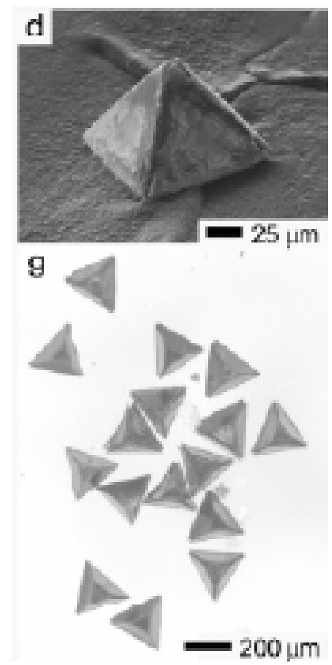
Case Study: Nano-liter Self-assembled Boxes

Controlled the shapes





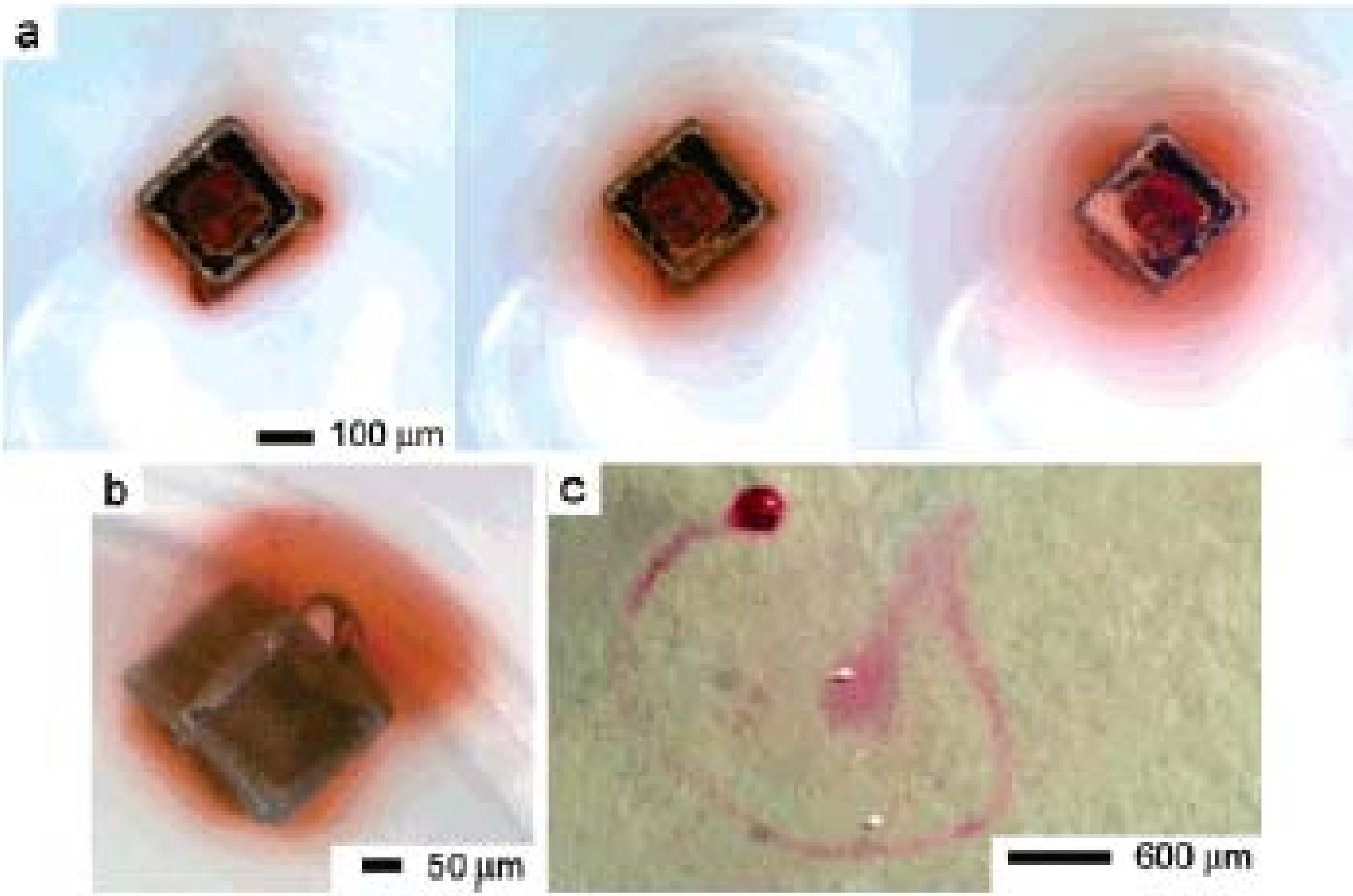




Leong et al., JACS, 2006

Case Study: Nano-liter Self-assembled Boxes

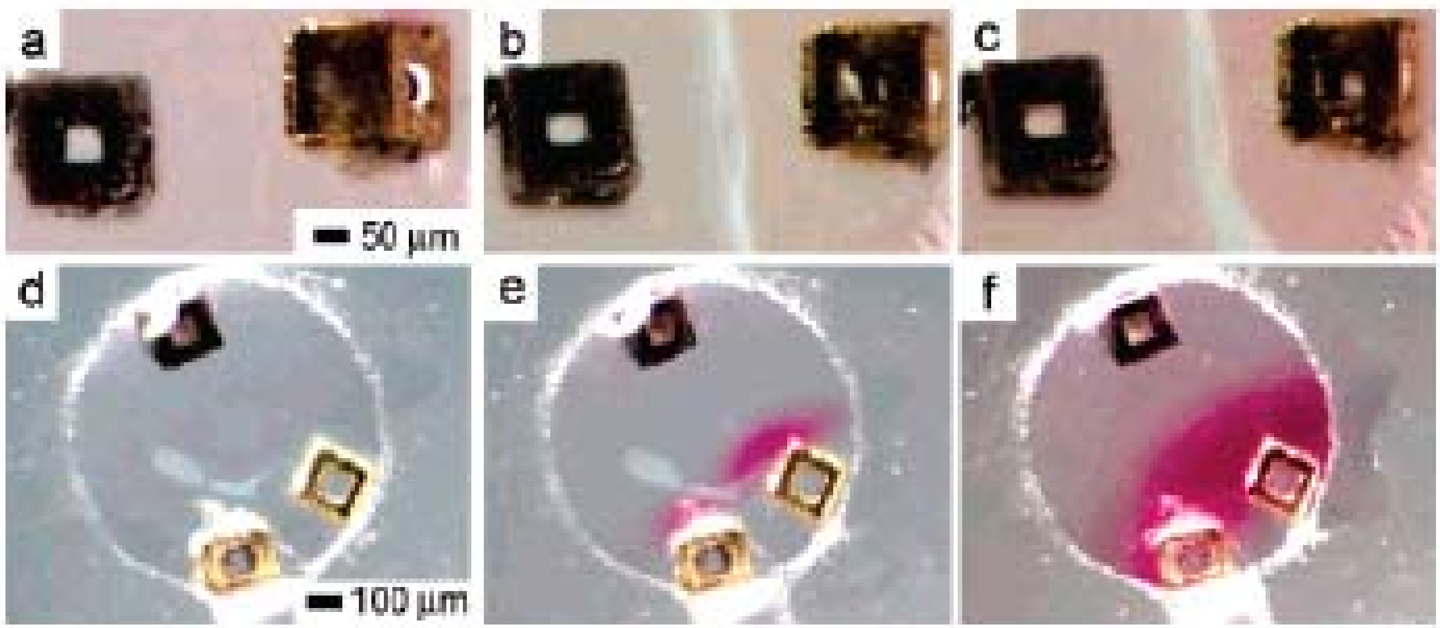
Controlled diffusion and release profiles



Leong et al., JACS, 2006

Case Study: Nano-liter Self-assembled Boxes

Controlled reactions



(a-c) reaction of copper sulfate and potassium hydroxide in an aqueous medium resulting in the formation of copper hydroxide along the central line between the containers; (d-f) the reaction of phenolphthalein (diffusing out of the two bottom containers) and potassium hydroxide (diffusing out of the top container) in an aqueous medium.

Leong et al., JACS, 2006

Lecture 2: Fundamentals and Theories of Self-Assembly

Final thought: Create or develop self-assembled structures at different scales

Nano- → Micro- → Macro-

Atoms, molecules, ●●● → Human, earth, ●●●