I. NANOFABRICATION AND CHARACTERIZATION

I. Nanofabrication and Characterization : TOC

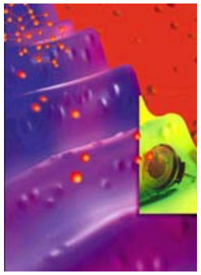
- Chap. 1 : Nanolithography
- **Chap. 2 : Self-Assembly**
- Chap. 3 : Scanning Probe Microscopy

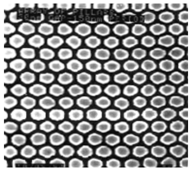
Chap. 2 : Self-Assembly

2.1 Introduction
2.2 Intermolecular Interactions
2.3 Self-Assembled Monolayers
2.4 Electrostatic Self-Assembly
2.5 Block Co-Polymers

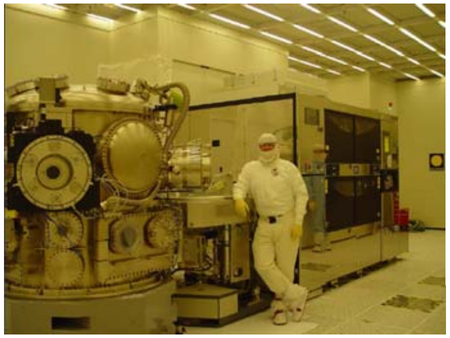
Nanoscale fabrication requirements

- Single nanometer scale resolution
- Patterning of large areas
- Uniformity
- Structural quality





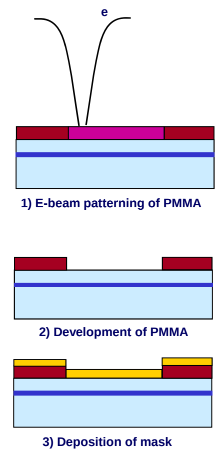
EUV lithography

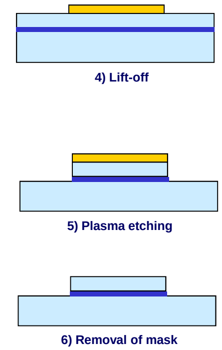


Sub-50 nm lithography now available in manufacturing environment

However, equipment is costly and not amenable to prototype research

E-beam lithography...

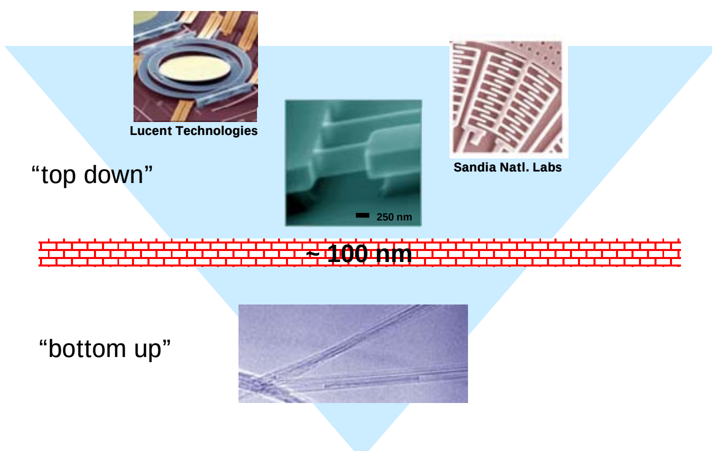




Cheaper, but also slower

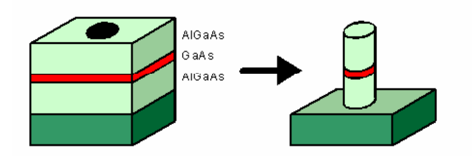
Not amenable to materials development

Need: Access to lower length scales

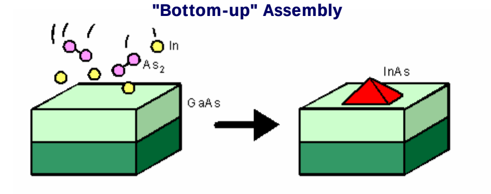


"Top Down" vs "Bottom-Up": Example

"Top-Down" Fabrication



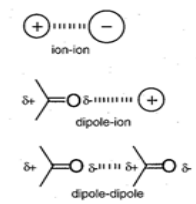
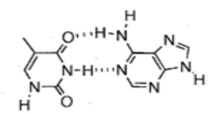
"Bottom-up" Assembly



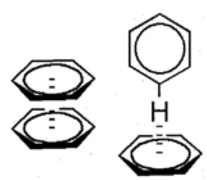
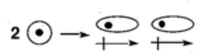
Ref: Dr. Marius Grundmann (http://sol.physik.tu-berlin.de)

Chap. 2 : Self-Assembly

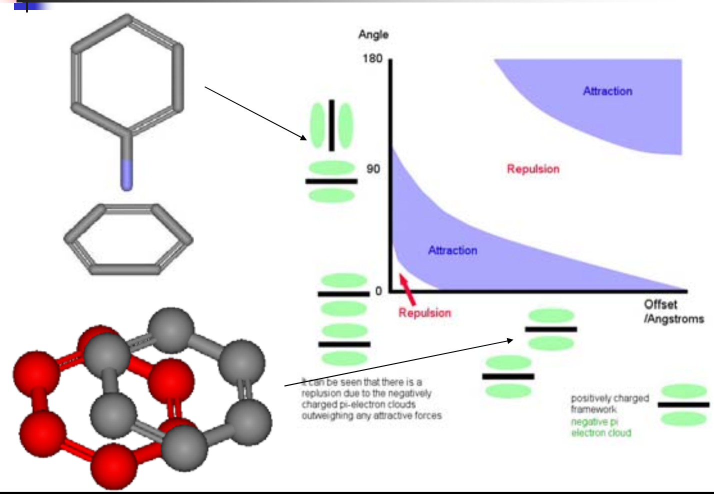
Types of intermolecular interactions

Type	Strength (kJ/mol)	Description	Example
Electrostatics	>190 (ion-ion) 40–120 (ion-dipole) 5–40 (dipole-dipole)	coulombic interactions between opposite charges	
Hydrogen bonding	15–40 (strong) 5–15 (moderate) <5(weak)	donor-acceptor interactions specifically involving hydrogen as the proton donor and a base as the proton acceptor	

Types of intermolecular interactions (ctnd)

Type	Strength (kJ/mol)	Description	Example
π-π Interactions	10–15 (face to face) 15–20 (edge to face)	attractive forces between electron-rich interior of an aromatic ring with the electron-poor exterior of an aromatic ring	
Dispersion forces	<5	momentary induced dipole-dipole interactions (also called London forces)	

Pi interactions...



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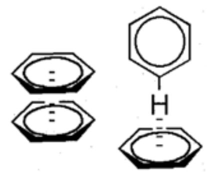
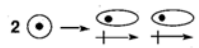
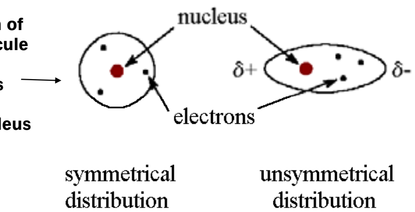
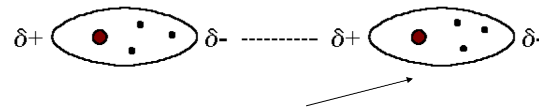
π-π Interactions	10–15 (face to face) 15–20 (edge to face)	attractive forces between electron-rich interior of an aromatic ring with the electron-poor exterior of an aromatic ring	
Dispersion forces	<5	momentary induced dipole-dipole interactions (also called London forces)	

London dispersion forces...

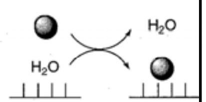
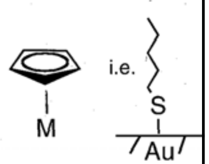
Because of the constant motion of the electrons, an atom or molecule can develop a temporary (instantaneous) dipole when its electrons are distributed unsymmetrically about the nucleus





A second atom or molecule, in turn, can be distorted by the appearance of the dipole in the first atom or molecule (because electrons repel one another) which leads to an electrostatic attraction between the two atoms or molecules.

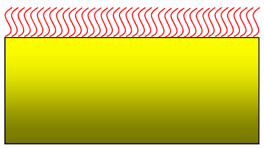
Types of intermolecular interactions (ctnd)

Type	Strength (kJ/mol)	Description	Example
Hydrophobic effects	varied 5–40	association of non-polar binding partners in an aqueous medium or vice versa	
Dative bonding	varied 20–380	coordination of a metal by a ligand donating two electrons	

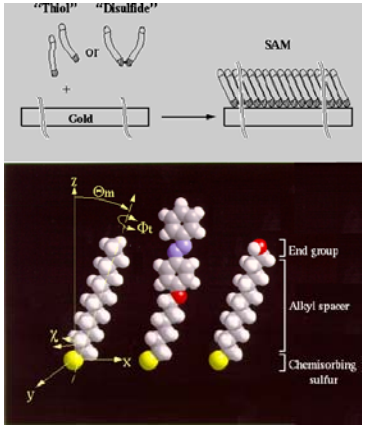
Chap. 2 : Self-Assembly

Self-assembled monolayers

- **"Self-assembly" refers to the deposition of an organized layer onto a substrate with with a high-degree of control and/or ordering.**
- **One common example are "Self-Assembled Monolayers" (SAMs): organic molecules that deposits from solution onto a substrate with a thickness of a single molecule and a well-defined orientation.**



Example: Thiols on Au

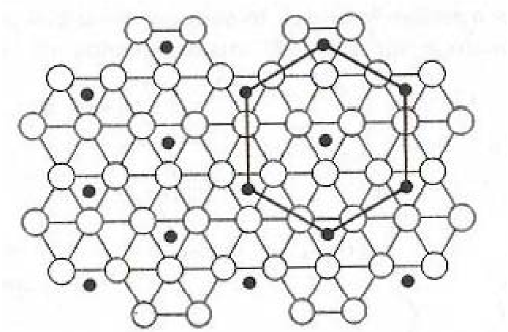


- **A thiol is a sulfur-containing organic compound with the general formula RSH where R is arbitrary. An example is ethyl mercaptan, C_2H_5SH.**
- **$CH_3(CH_2)_nSH$, n=1,3,5,7,9,11,15,17,21; can form closely packed stable SAMs on gold.**
- **It is believed that the terminal H atom is removed and S forms a covalent bond with the gold surface.**

Source: IBM Zurich

For more info on thiols, check out: LSU

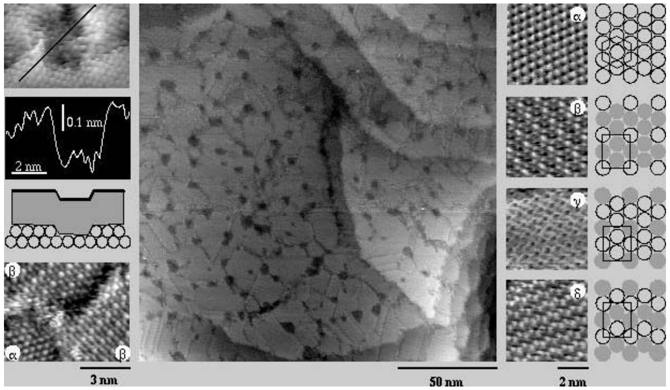
Organization of thiols SAMs on Au



Postulated adsorption pattern of a thiol on Au (111)

Thiol molecules form an hexagonal lattice

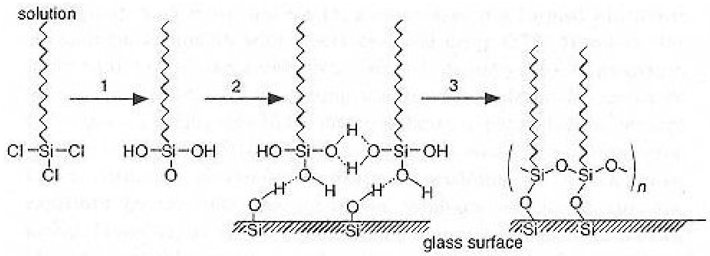
Dodecanethiolthiol on Au



STM image of dodecanethiol on gold(111). Molecular arrangements are hexagonal with an addtional rectangular superlattice (right).

Source: IBM Zurich **For more images of thiols on Au, check out: Weiss Group, Penn State**

Silanes

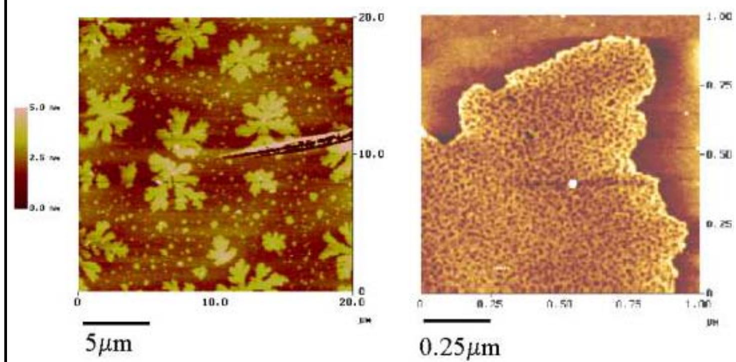


The silane-terminated molecule will form SAMs on oxide surfaces

Heavily studied in Si technology

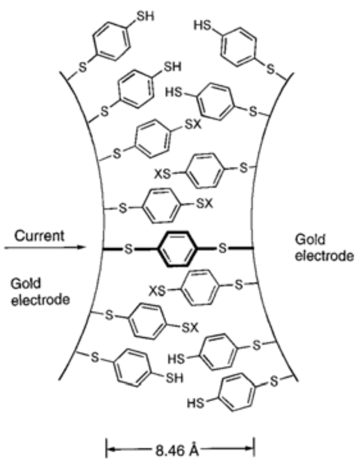
Shown: Octadecyltrichlorosilane on Si

ODS submonolayer on Si

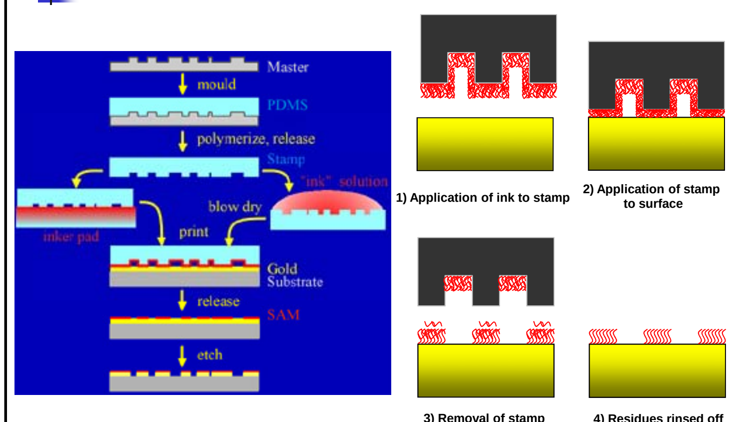


Source: Borguet group, U Pittsburgh

SAM-based molecular junction

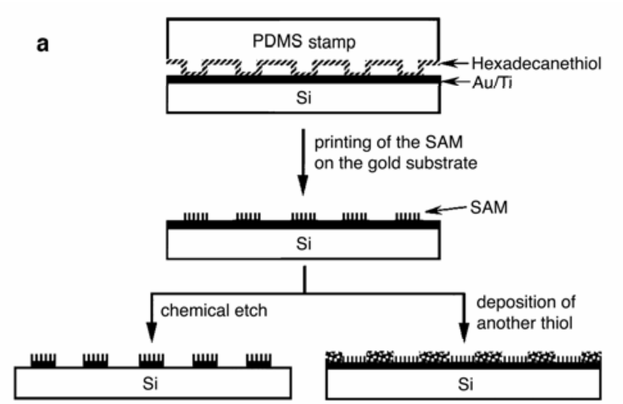


Patterning of SAMS by micro-contact printing

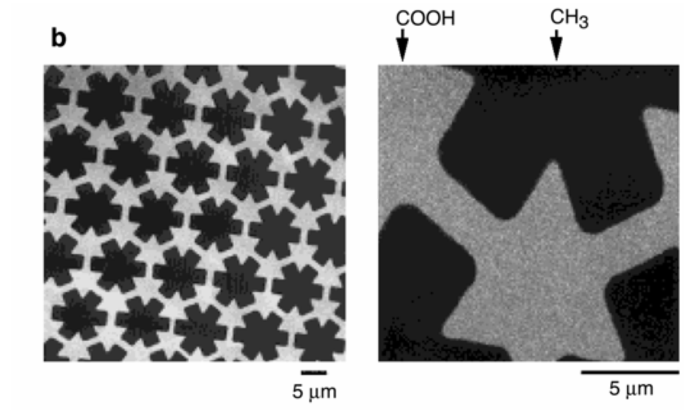


Source: IBM Zurich

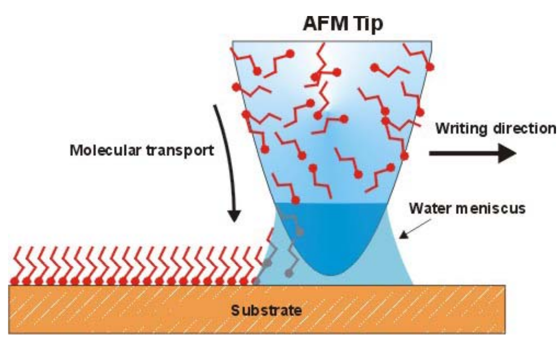
Patterning of SAMS by micro-contact... (ctnd.)



Patterning of SAMS by micro-contact... (ctnd.)

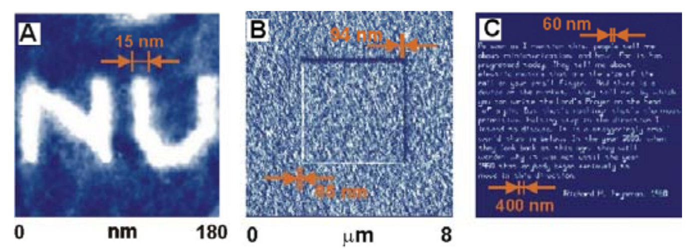


Patterning of SAMS by dip-pen lithography



Source: Mirkin Group, NWU

Patterning of SAMs by dip-pen lithography

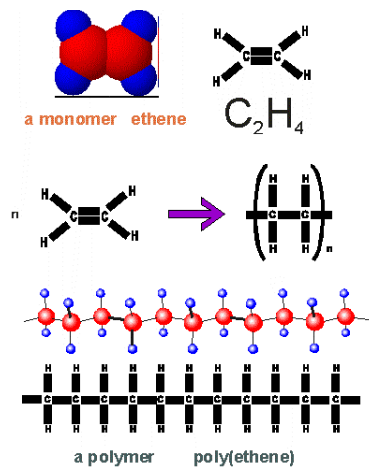


A) Ultra-high resolution pattern of mercaptohexadecanoic acid on atomically-flat gold surface. **B)** DPN generated multi-component nanostructure with two aligned alkanethiol patterns. **C)** Richard Feynmann's historic speech written using the DPN nanoplotter

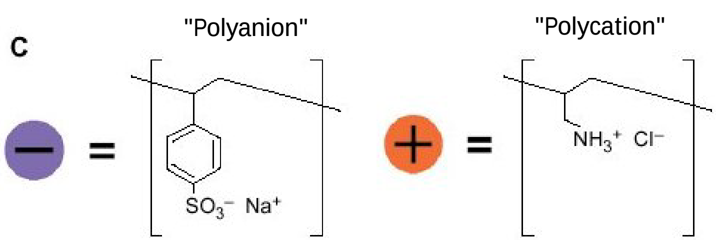
Source: Mirkin Group, NWU

Chap. 2 : Self-Assembly

Monomers and Polymers

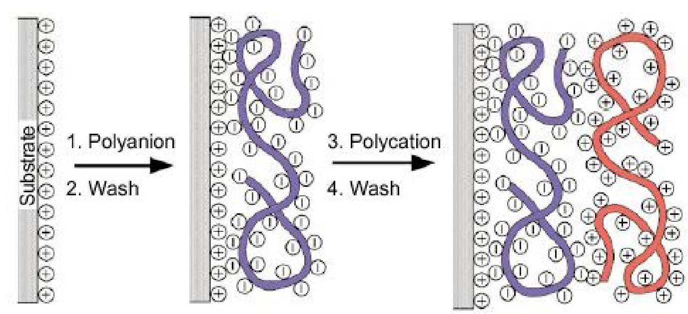


Ionic monomers



- Different monomers will exhibit different ionic properties
- For example, the sodium salt of poly(styrene sulfonate) will be negatively charged, while poly(allylamine hydrochloride) will be positively charged.

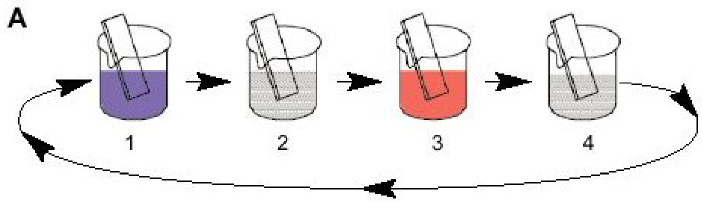
Ionic layer-by-layer (LBL) self-assembly



These ionic properties enable the controlled successive stacking of single layers of each polyion

Want more ? Google it !

Synthesis of polyionic multilayer structures

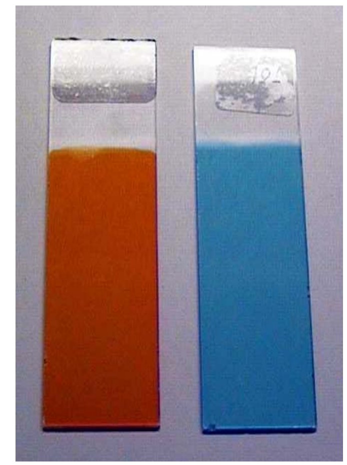


- Steps 1 and 3 represent the adsorption of a polyanion and polycation, respectively, and steps 2 and 4 are washing steps.
- The four steps are the basic buildup sequence for the simplest film architecture, $(a/b)_n$.
- The construction of more complex film architectures requires only additional beakers and a different deposition sequence.
- Layers of controlled thickness can be deposited with typical deposition time of one minute per layer.

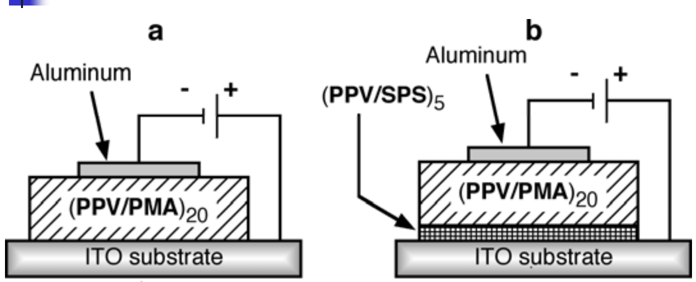
Growth of LBL ISAMs on glass slides

- Exceptionally homogeneous films can be deposited on substrates of arbitrary size and shape
- Substrate can be glass, mica, plastic, metal, etc.

Source: Heflin Group, Virginia Tech

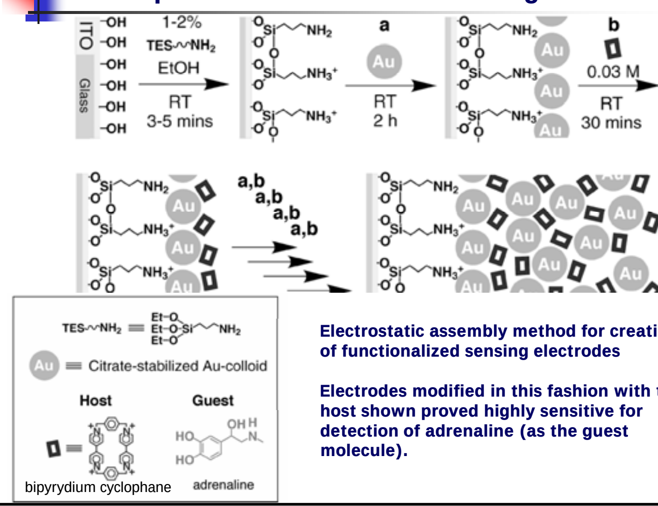


LBL films for light-emitting diodes



LBL engineering of a light-emitting device: (a) Multilayer of PPV/PMA performs similarly to PPV alone. (b) Combined architecture of PPV/PMA multilayer on top of PPV/SPS multilayer allows better hole-transport between the PPV/PMA and the ITO anode, and results in enhanced electroluminescence.

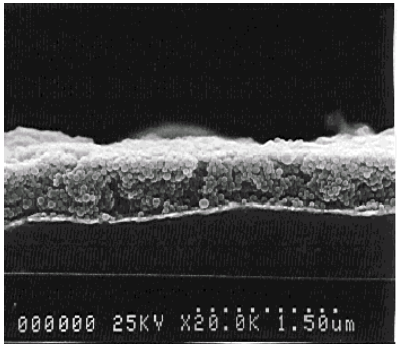
LBL/particle assemblies for sensing electrodes



Electrostatic assembly method for creation of functionalized sensing electrodes

Electrodes modified in this fashion with the host shown proved highly sensitive for detection of adrenaline (as the guest molecule).

Polyion – nanosphere assemblies

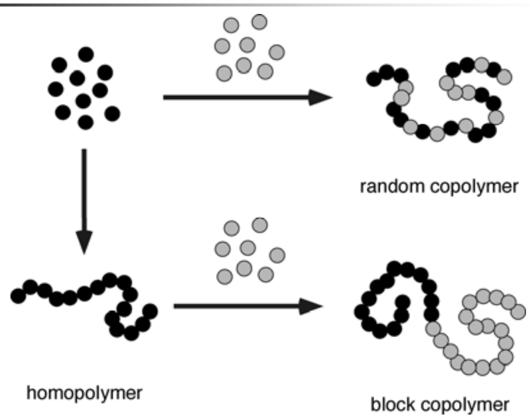


Ionic film grown by successive assembly of poly(dimethyldiallylammonium chloride) (PDDA) and 45-nm silica spheres

Source: Lvov Group, La Tech

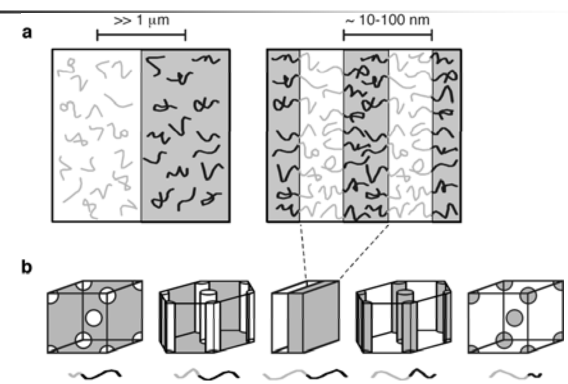
Chap. 2 : Self-Assembly

Synthesis of block copolymer



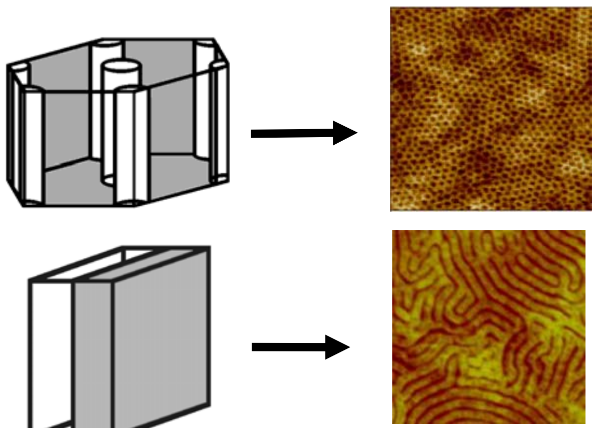
Schematic illustration of the synthetic routes to homopolymers, random copolymers, and block copolymers.

Microphase separation of block copolymers



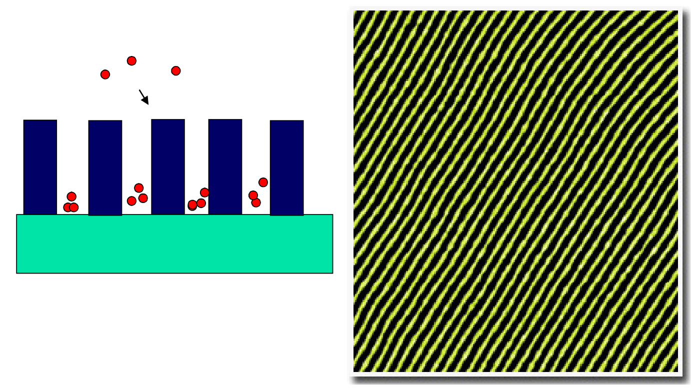
(a) A blend of two incompatible homopolymer separates into distinct phases on a large scale (left), whereas block copolymers *micro*phase separate into periodic domains(right). (b) Basic morphologies obtained by different block copolymer compositions.

Microphase separation of block copolymers (ctnd.)



Top view AFM images of microphase separation
in block copolymer thin films

Application: synthesis of nanowires



Microphase separated structure used as template for growth of nanowires

Application: nanofabrication of nanowires