Textbook: Introduction to Nanoscience and Nanotechnology

Chap. 2 Self-Assembly and Self-Organization

2.1 Advantages of Self-Assembly

- For material fabrication,
  top-down approach: a rough, large scale materials -> a shape into it
  bottom-up approach: simple building blocks in a pre-designed scheme-> assembly

- Miniaturization of electrical components (a fundamental demand for high-speed operation):
  1) top-down approach has been extensively employed up to sub micrometers (a few tens of nanometers) in microelectronics industries, following the Moore's law,
     but has inherent limitations of shorter wavelengths, formation of 3-dimensional structures.
  2) bottom-up methodology (molecular self-assembly) provides a direct access to the nanometer regime; molecular building blocks that assemble spontaneously into defined, desired structures -> The main challenge is the assembly process!

2.2 Intermolecular Interactions and Molecular Recognition

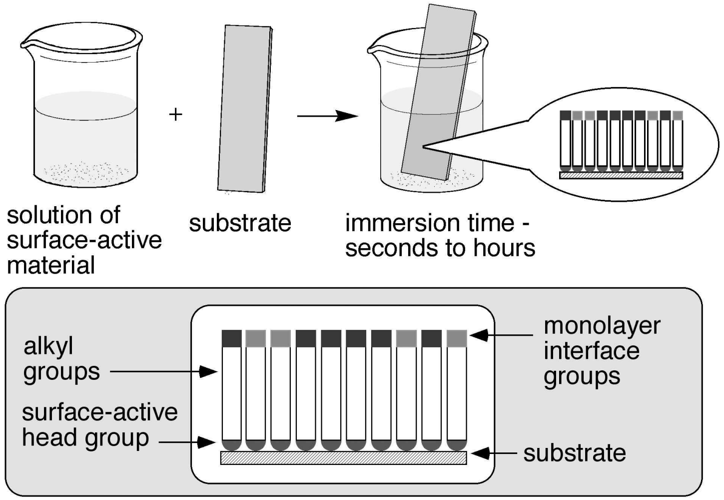
- Intermolecular Interactions (see, TABLE 2.1):
  1) Electrostatics; Coulomb interactions between opposite charges
  2) Hydrogen bonding; donor-acceptor interactions specifically involving hydrogen as the proton donor and a base as the proton acceptor
  3) $\pi-\pi$ interactions; attractive forces between electron-rich interior of an aromatic ring with

the electron-poor exterior of an aromatic ring
4) Dispersion forces; momentary induced dipole-dipole interactions (London forces)
5) Hydrophobic effects: association of non-polar binding partners in an aqueous medium or vice versa

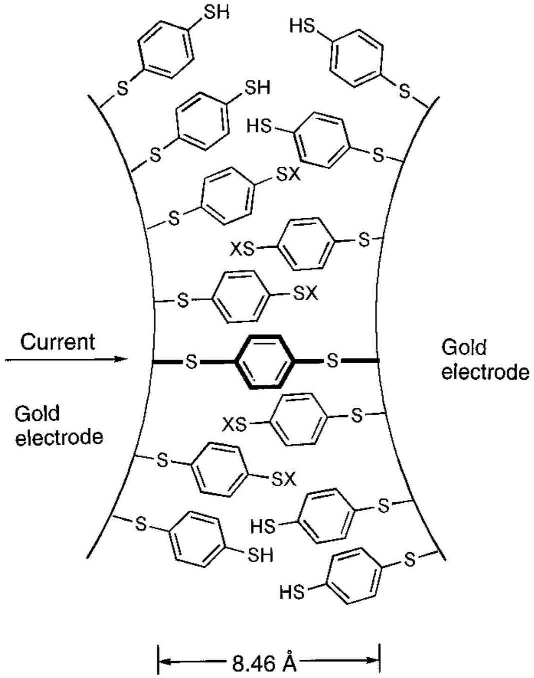
[Key Issue] How to incorporate molecular recognition and molecular programming into macromolecular nanoscale systems and to extend the order into the macroscale regime.

2.3 Self-Assembled Monolayers (SAMs)

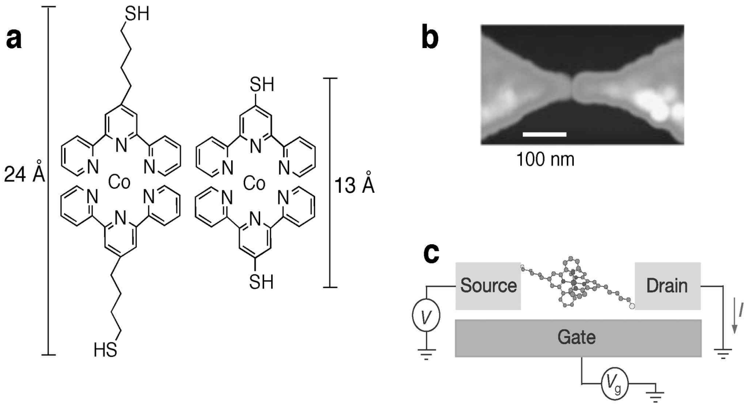
- A spontaneous chemisorption process: *surface-active* head group



- Molecular junction (bet Au electrodes)



- Single atom transistor
  (Cobalt coordinated terpyridine thiols)



- STM patterning of SAMs

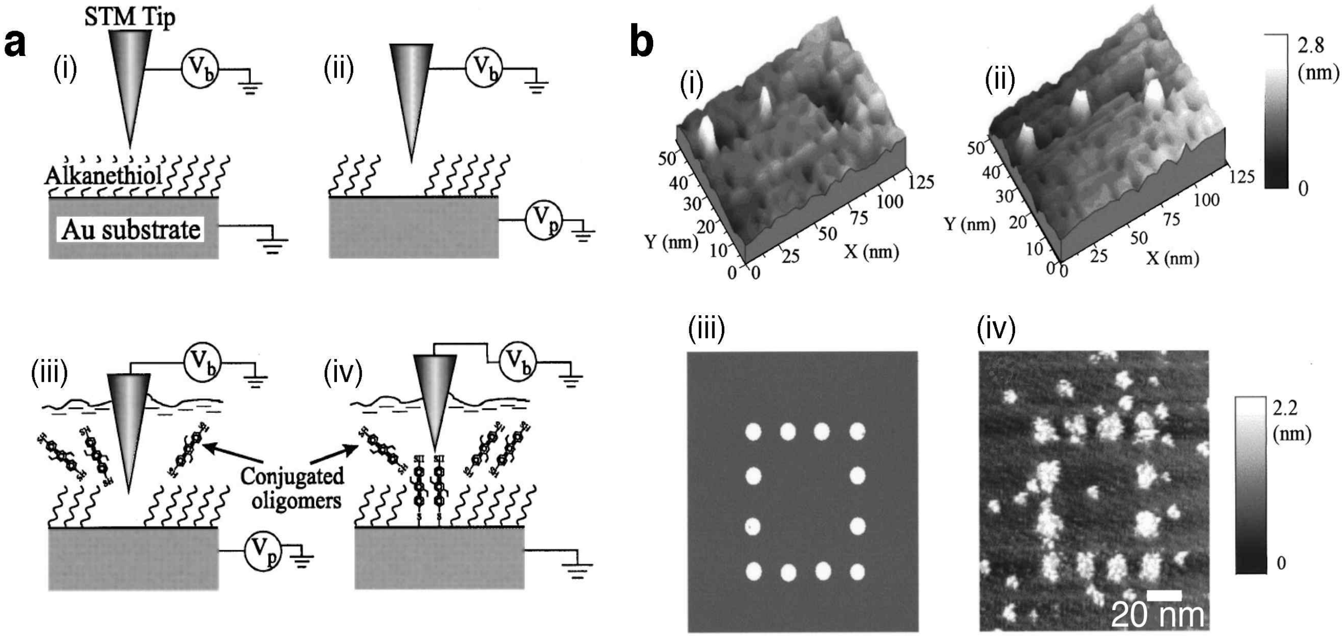


Figure 2.5. (a) A schematic representation of the STM patterning of SAMs. (i) Normal STM imaging of the SAM with tip bias V_b; (ii) Removal of SAM by applying a pulse V_p to the gold substrate; (iii) The same as (ii) in solution of conjugated oligomers; (iv) insertion of conjugated oligomers in the patterened sites. (b) STM image of dodecanthiol and conjugated oligomeric patterned SAMs. (i) The STM image after consecutive pulsing at three different locations indicating insertion of molecules (two peaks) and one pit without insertion. (ii) The same region imaged a few minutes later showing adsorption into the remaining pit. (iii) A programmed pattern consisting of circles tracing out a rectangle. (iv) The resulting image of the patterned dodecanthiol SAM after chemisorption of the conjugated oligomers showing the produced rectangular frame. (From Ref. 13 by permission of American Institute of Physics.)

- Microcontact Printing (uCP)

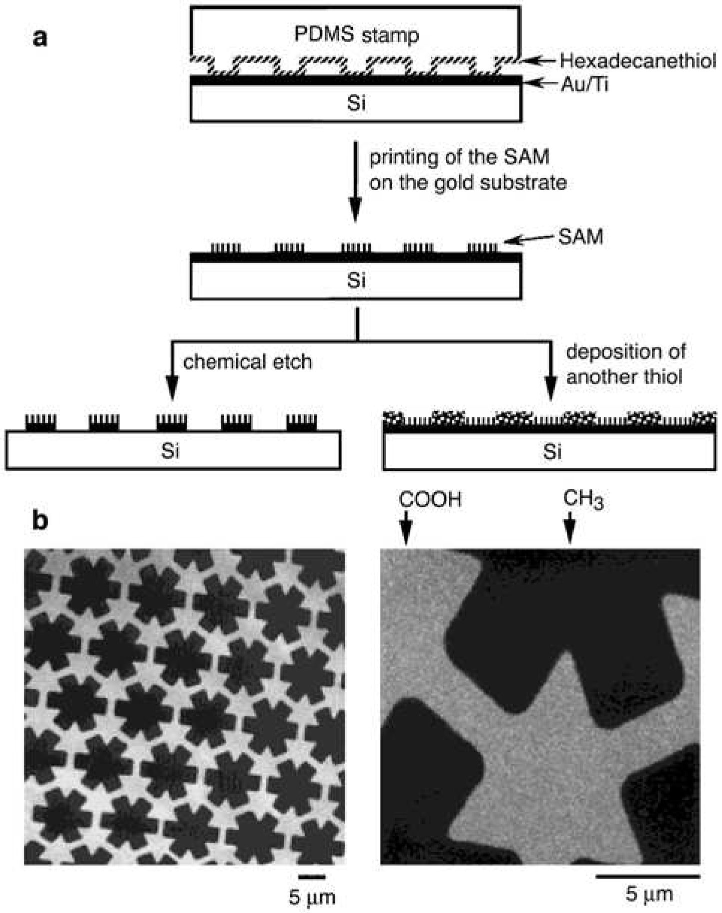
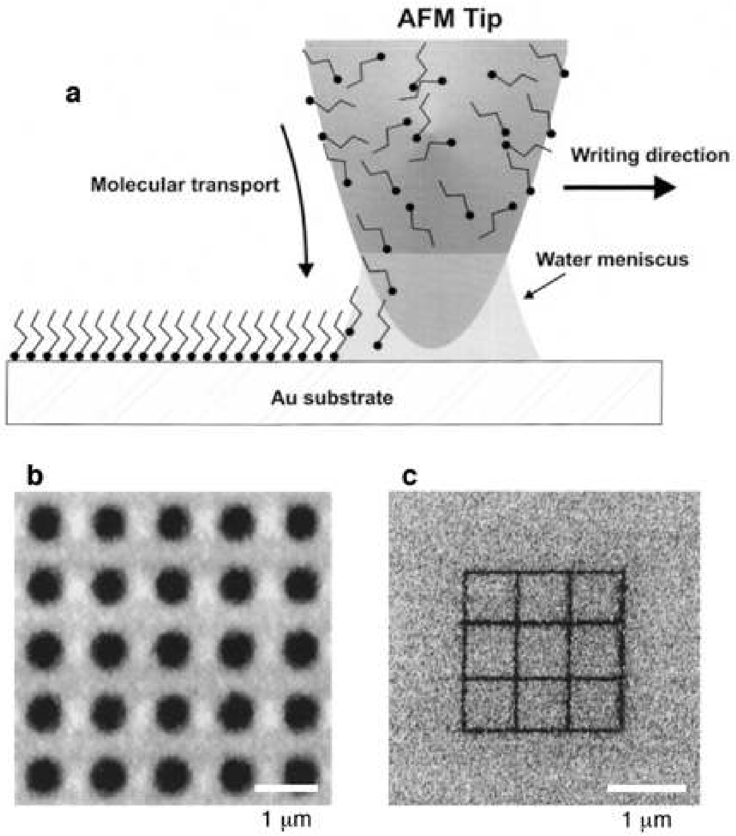


Figure 2.7. (a) Schematic illustration of the µCP procedure for patterning an alkanethiol (hexadecanethiol-HDT) on a flat gold substrate. (b) Lateral force microscope (LFM) images (at two different magnifications) of a patterned gold substrate with SAMs terminated in chemically different head groups (HDT-CH$_3$ and16-mercaptohexadecanoic acid-COOH). The image contrast results from differences in frictional forces between the surface and the probe tip. Carboxylic acid terminated SAM show high measured frictional forces (light regions) and methyl terminated SAM show low measured frictional forces (dark regions). (From Ref. 12 by permission of WILEY-VCH Verlag GmbH & Co.)

- Dip-pen nanolithography (DPN)

Figure 2.8. (a) Schematic representation of dip-pen nanolithography (DPN). A water meniscus formed between AFM tip and the gold substrate directs the thiol molecules onto the substrate. The size of the water meniscus is controlled by the relative humidity that in turn affects the overall resolution of DPN. (b) LFM image of an array of octadecanethiol dots on a gold surface generated by holding an ODT-coated AFM tip in contact with the surface for ca. 20 s. (c) LFM image of a molecule-based grid consisting of eight lines 100 nm in width and 2 μm in length. (From Ref. 17 by permission of American Association for the Advancement of Science.)



- Nanotransfer printing (NTP)

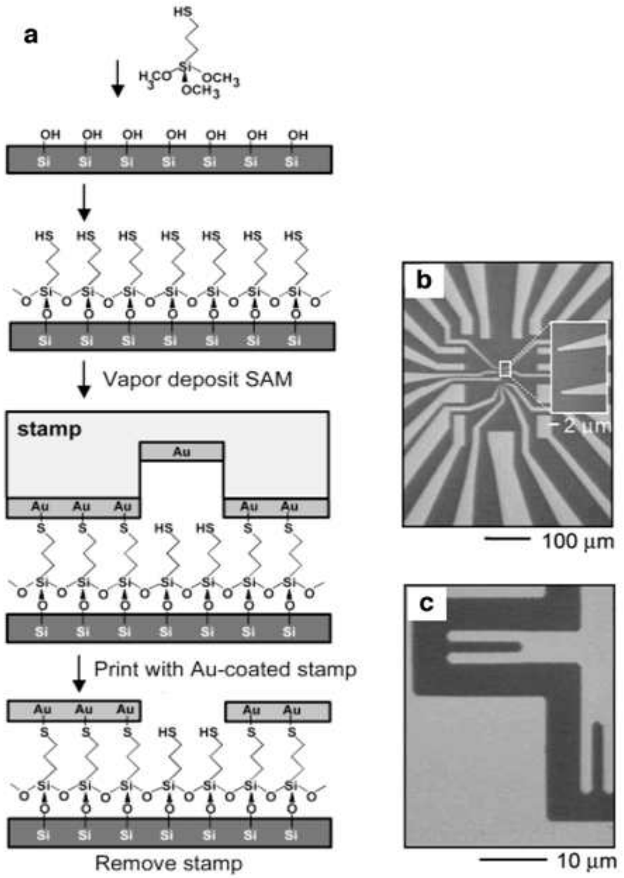


Figure 2.9. (a) Schematic representation of the nanotransfer printing (nTP) procedure to create gold patterns on Si substrates. Optical micrographs of a gold pattern formed by nTP on (b) a silica wafer, and (c) a plastic sheet [organosilsesquioxane modified poly(ethylene terephthalate)], demonstrating the wide applicability of the technique. (From Ref. 18 by permission of American Chemical Society.)

2.4 Electrostatic Self-Assembly

- Layer-by-Layer Deposition (LBL)

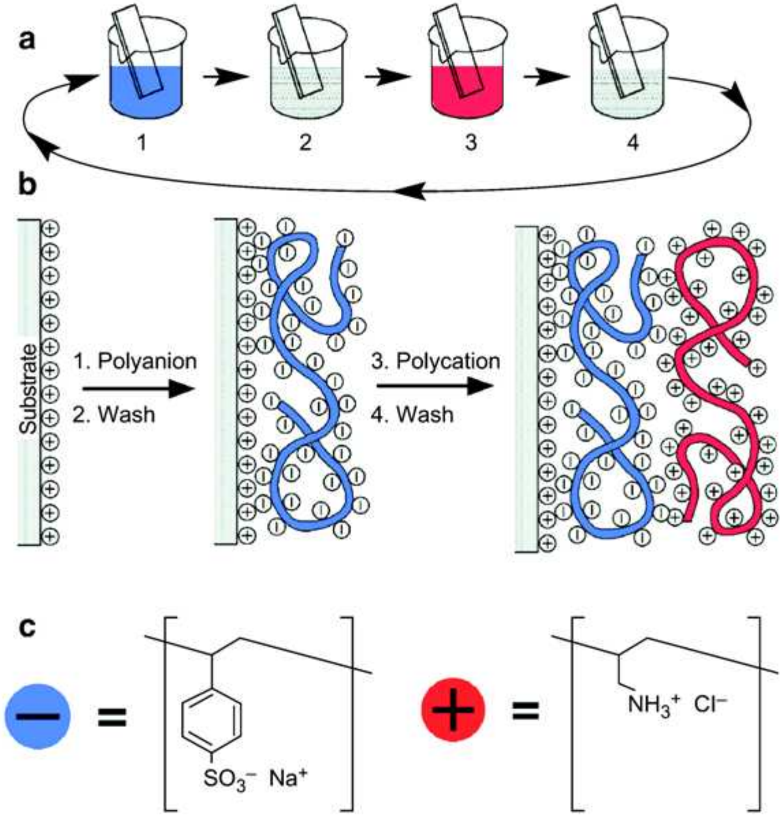


Figure 2.11. Film growth by the LBL technique: (a) Repeated dipping of a charged-surface slide into polyanion and polycation solutions (steps 1 and 3, respectively) with intermediate washing steps (2 and 4) results in alternate deposition of the corresponding polyions (b). (c) Chemical structures of two typical polyions: sulfonated polystyrene (SPS) and poly(allylamine hydrochloride) (PAH). (From Ref. 25 by permission of American Association for the Advancement of Science.)

- LBL with metallic nanoparticles for sensing applications

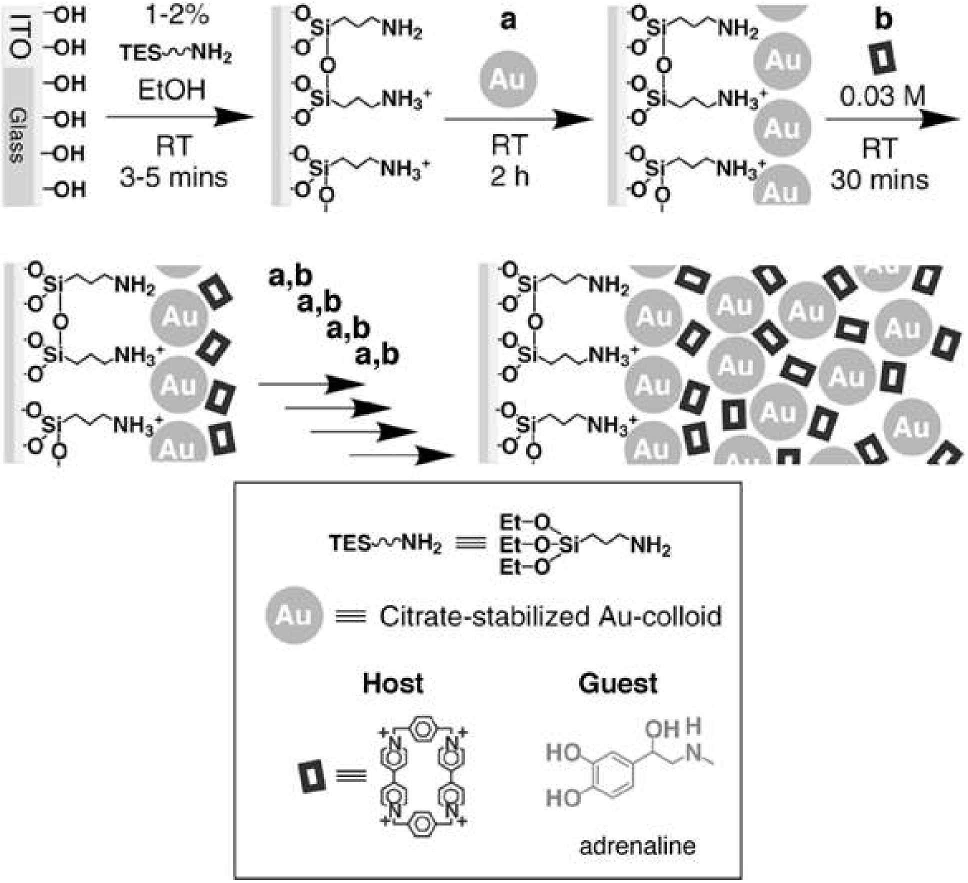


Figure 2.13. Electrostatic assembly method for creation of functionalized sensing electrodes: alternating deposition steps of (a) negatively charged gold nanoparticles, and (b) positively charged host molecules. Electrodes modified in this fashion with the host shown proved highly sensitive for detection of adrenaline (as the guest molecule). (From Ref. 33 by permission of WILEY-VCH Verlag GmbH & Co.)

- 3-D nanocomposites; polymer capsules, DNA directed-assembly

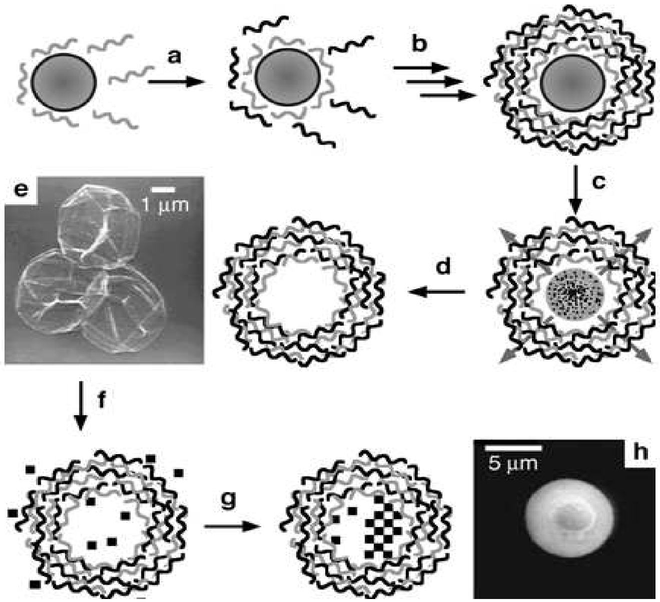


Figure 2.14. Polymer capsules: Consecutive adsorption of positively (grey) and negatively (black) charged polyelectrolytes onto negatively charged particles (a,b) and subsequent decomposition of the colloidal core (c,d) yields a suspension of hollow polyelectrolyte capsules (e, TEM image). Addition of crystalline molecules bearing charged groups (f) and changing the ionic or solvent composition drives the molecules into the capsules, where nucleation centers form and crystals are grown. (h) TEM image of a volume-confined crystal of 6-carboxyfluorescein grown inside a capsule that was based on discocyte biocolloid. (From Refs. 35 and 37 by permission of WILEY-VCH Verlag GmbH & Co.)

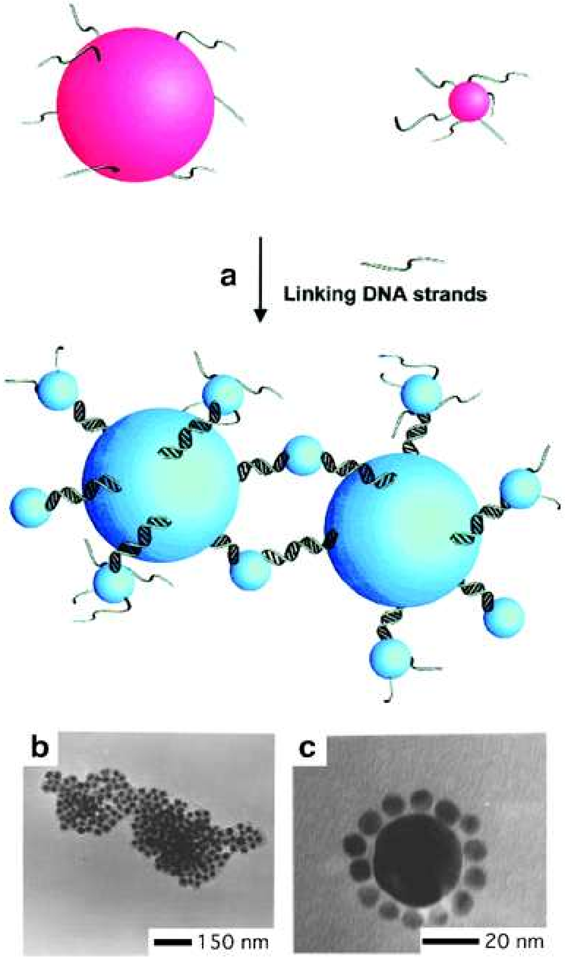


Figure 2.15. (a) DNA-directed assembly strategy for preparation of network materials from two different-sized oligonucleotide-functionalized nanoparticles. TEM images of: (b) Aggregate formed by linking 8-nm and 31-nm gold nanoparticles, (c) "Satellite" structure obtained in 120-fold excess of the 8-nm colloids. (From *Inorg. Chem.* **39**(11), 2258-2272 (2000) by permission of American Chemical Society and Ref. 41 by permission of American Chemical Society.)

2.5 Self-Organization of Block-Copolymers

- Homopolymers, random copolymers, block copolymers

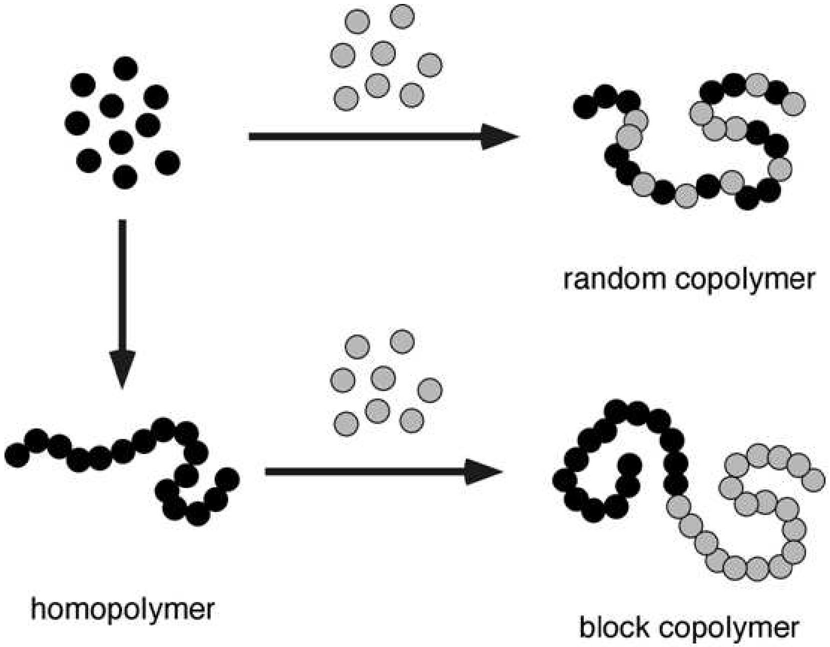


Figure 2.17. Schematic illustration of the synthetic routes to homopolymers, random copolymers, and block copolymers.

- Phase behaviors of different polymers

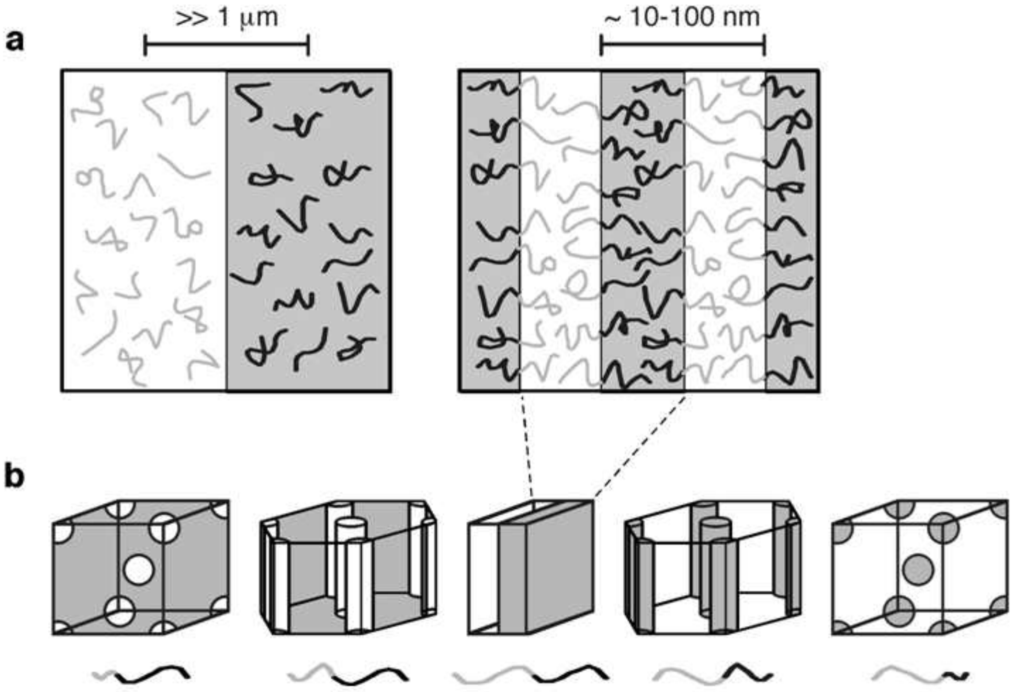


Figure 2.18. (a) Fundamental differences in phase behavior of different polymers: A blend of two incompatible homopolymer separates into distinct phases on a large scale (left), whereas block copolymers *micro*phase separate into periodic domains on the scale of a single polymer strand (right). (b) Basic morphologies obtained by different block copolymer compositions.

- Metal nanowire formation

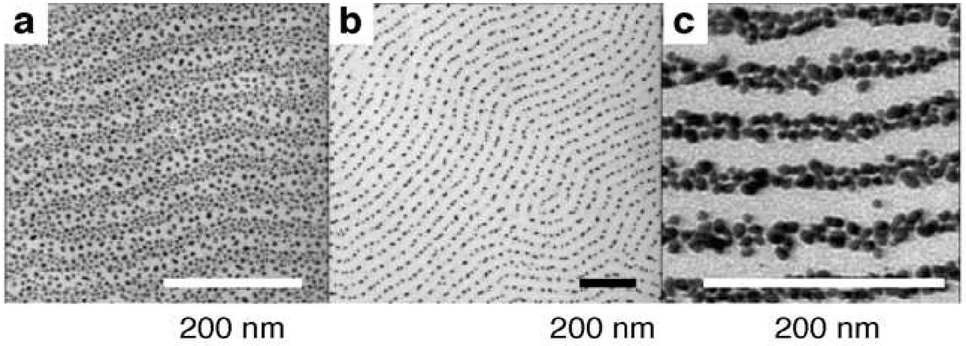


Figure 2.19. Metal nanowire formation using a block copolymer template: Shown are TEM images of: (a) Gold metal vapor-deposited onto a preformed PS-*b*-PMMA template. (b) After annealing at 180 °C for 1 min., gold nanoparticles segregate selectively to the PS domains and form chains. (c) Repeated deposition and short-time annealing increases the metal loading, forming continuous conductive nanowires. (From Ref. 54 by permission of Macmillan Magazines Ltd.)

[Homework/Reading Assignment]

1. Whitesides, G. M. et. al, Self-assembly all scales, *Science*, 295, 2418 (2002).
2. Galow T. H. et. al, A “building block approach”, *Adv. Mat.* 12, 576 (2000).