Chap. 12 Self-Assembled Future

12.1 Introduction

- The ultimate goal of nanotechnology is to self-assemble molecules – the way we desire, in order to manipulate nature.

12.2 Definition: Self-Assembled Future

- Self-assembly can be defined as a process by which atoms, molecules, or particles spontaneously aggregate into organized structures (without the use of external forces). We humans would like to control this process in order to design and synthesize new desired structures – like enzymes, proteins, DNA, and the cell's organelles.

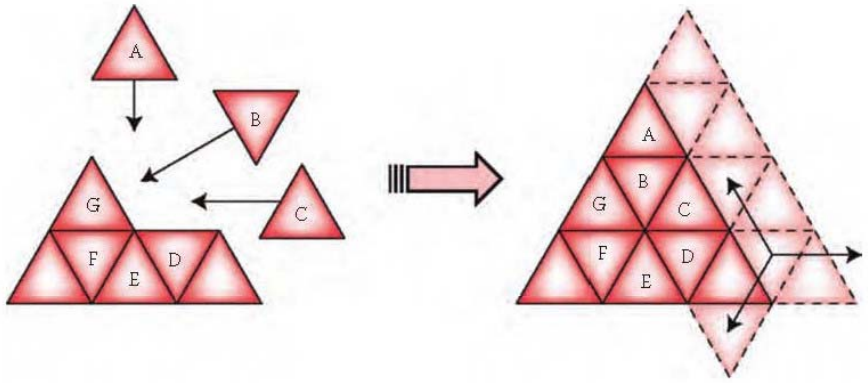

Figure 12.1 Illustration of the self-assembly process. Molecules A, B, C are disordered above underlying structure DEFG. These molecules spontaneously assemble into an ordered structure ABCDEFG. Dotted triangles are the addition of future molecules that grow the structure different directions as shown by the arrows.

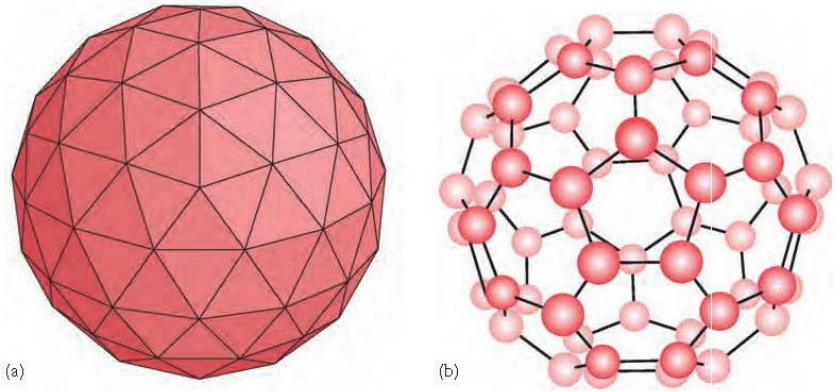

Figure 12.2 Illustration of a 3-D macroscopic geodesic dome. [Adapted from Wikimedia Commons.] (a) and nanoscopic buckyball C60 molecule (b).

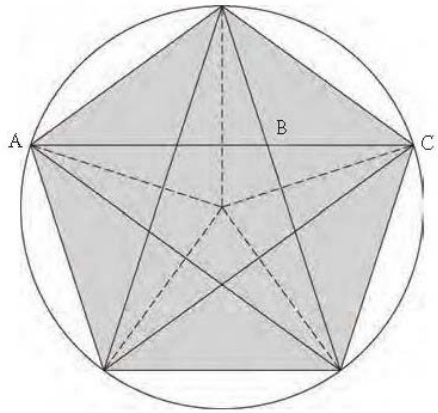

Figure 12.3 Illustration of pentagon that encapsulates a five-pointed star. Line ABC is one of the lines in the star. There are five equilateral triangles (dotted lines) within the pentagon and star. Line ABC determines the size of the pentagon inscribed in the circle.

12.4 Chemical Assembly Definition: Self-Assembled Future

- Two types: static and dynamic

- Static chemical assembly is an equilibrium process that is determined by chemical thermodynamics. It produces equilibrium reactions that are based on such chemical forces as hydrogen bonding, electrostatics, and van der Waals forces.

- Dynamic self-assembly is a non-equilibrium process that is determined by the kinetics of reactions (how fast reactions reach chemical equilibrium).

- What determines whether self-assembly will occur?
  It is the change in free energy between molecular products and the reactants.

  CO_2 (product) from C and O_2 (reactants): $C(s) + O_2(g) + CO_2(g)$

- Chemical thermodynamics: free energy, entropy, enthalpy (heat)

12.4.1 Free Energy

- The free energy change (ΔF) is defined as the driving force for doing useful work at a constant temperature and constant pressure (usually 298 K [25^0C] and 1 atm pressure).

- At equilibrium, $\Delta F = 0$

- Gibbs-Helmholtz Equation: $\Delta F = \Delta H - T\Delta S$
  *Change in heat of the reaction (ΔH) and change in entropy (ΔS) between products and reactants

  *Entropy is defined as a measure of disorder (randomness) in atoms, molecules, or components.
  *Enthalpy comes from the Greek word *en* ('put into") plus *thalpein* ("heat"): when ΔH is positive, heat is absorbed.

12.5 Snowflake Assembly

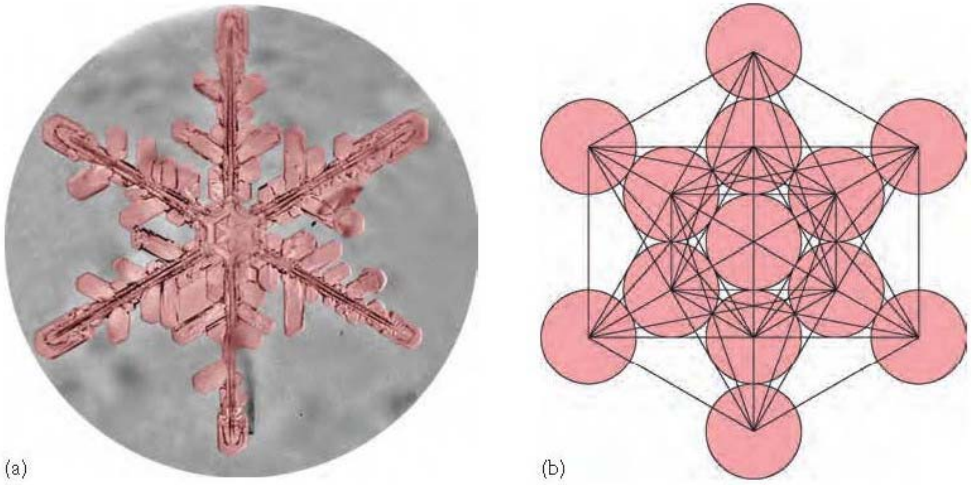

Figure 12.7 (a) Photograph of a snowflake taken under a low-powered optical microscope [Courtesy of Cammer, M., Wikimedia Commons.], and (b) illustration of Metatron's cube [Courtesy of Deathlime, Wikimedia Commons.]. Both are examples of sixfold symmetry and close-pack hexagonal arrangement of atoms.

12.8 Spiral-Step Assembly

- A spiral-step of atoms occurs due to line defects in solids, called screw dislocations.

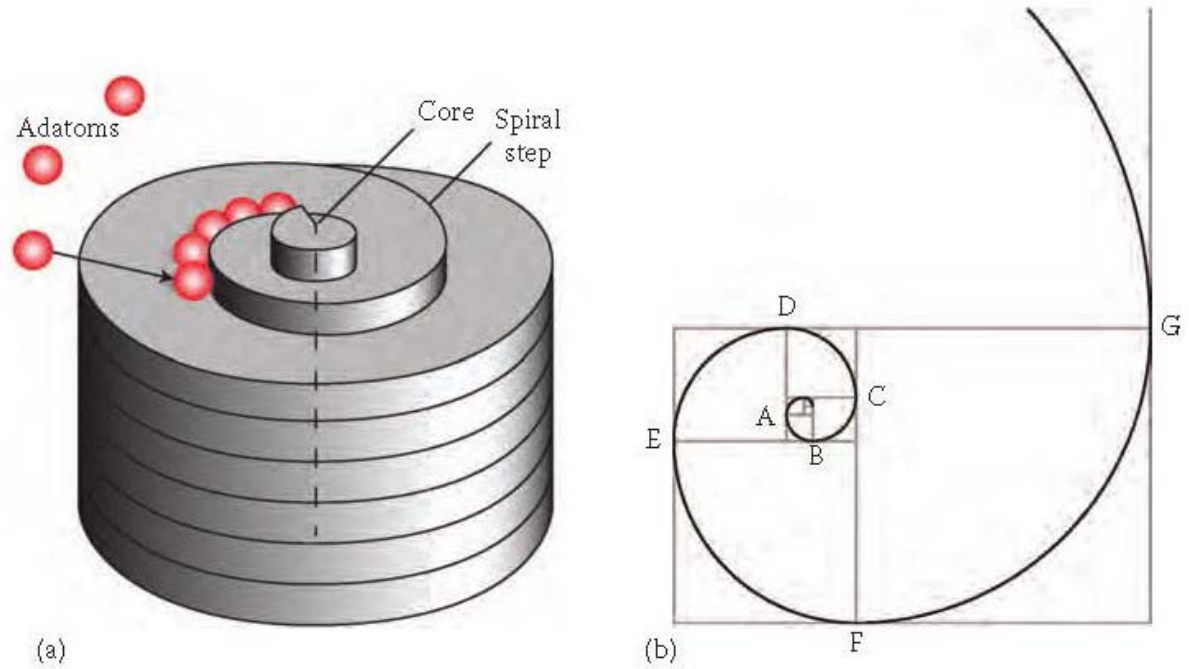

Figure 12.11 Illustration of (a) 3-D counterclockwise spiral step. [Adapted from Hannon, J.B. et al., *Science*, 313, 1266, September 1, 2006.] and (b) 2-D top view of the spiral as it winds around a central core. Adatoms deposit onto the spiral step at **the jog sites**, which cause the spiral to turn like a screw. [Adapted from Knott, R., Fibonacci num-

12.9 Amphiphilic Structures

- Cell membranes have two layers of micelles, which are self-assembled into "bilayers".
- Spherical bilayer vesicles are also called liposomes.

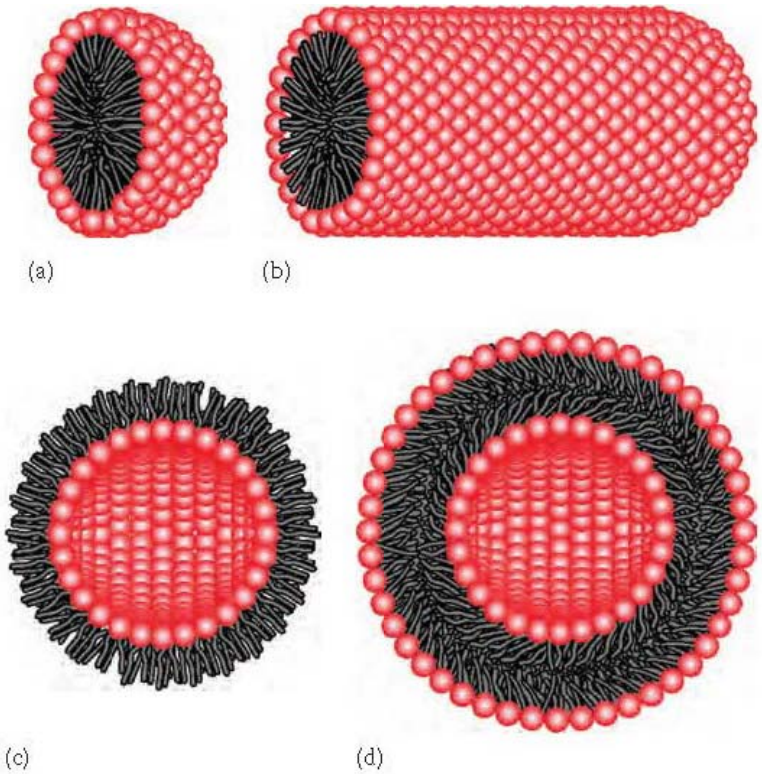

Figure 12.12 Illustrations of self-assembled amphiphiles: (a) a spherical micelle, (b) cylindrical micelle, (c) inverted micelle, and (d) spherical bilayer vesicle (liposome). [Adapted from Evans, D.F. and Wennerstrom, H., *The Colloidal*

- A fatty acid (or water) droplet in water (or fatty acid) environment

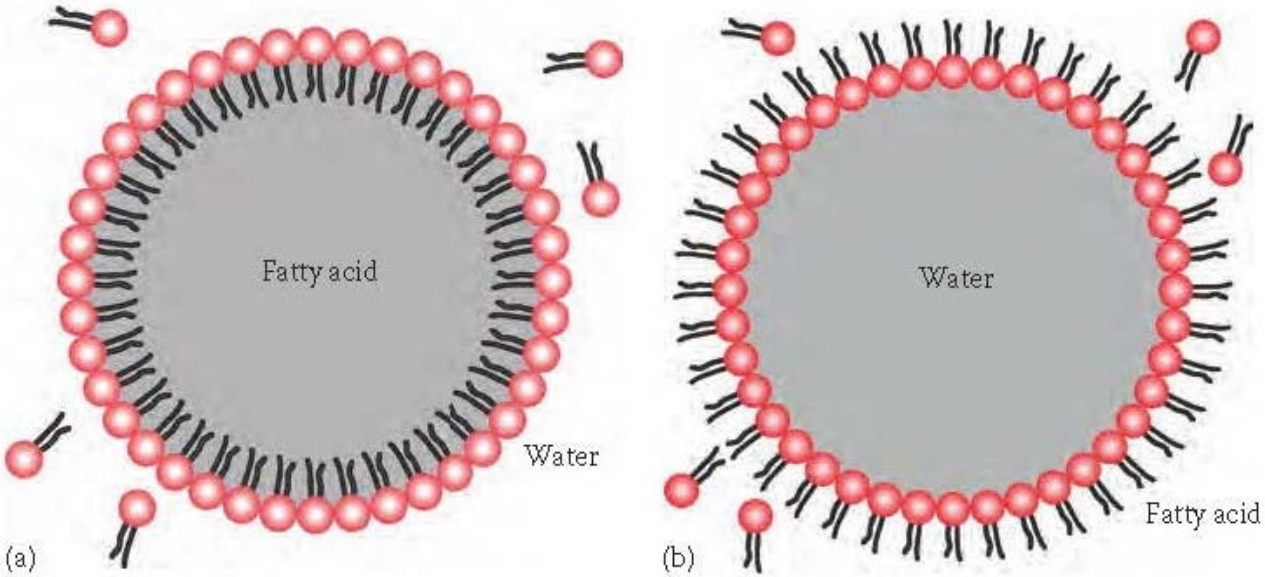

Figure 12.13 Illustration of manipulating water–fat interface, where (a) the polar heads of the fat droplets are surrounded by water (Case I), and (b) the polar heads of the fat medium surround the water droplets (Case II). [Adapted

12.10 Biomolecular Assembly

12.10.1 DNA Nanotube Assembly

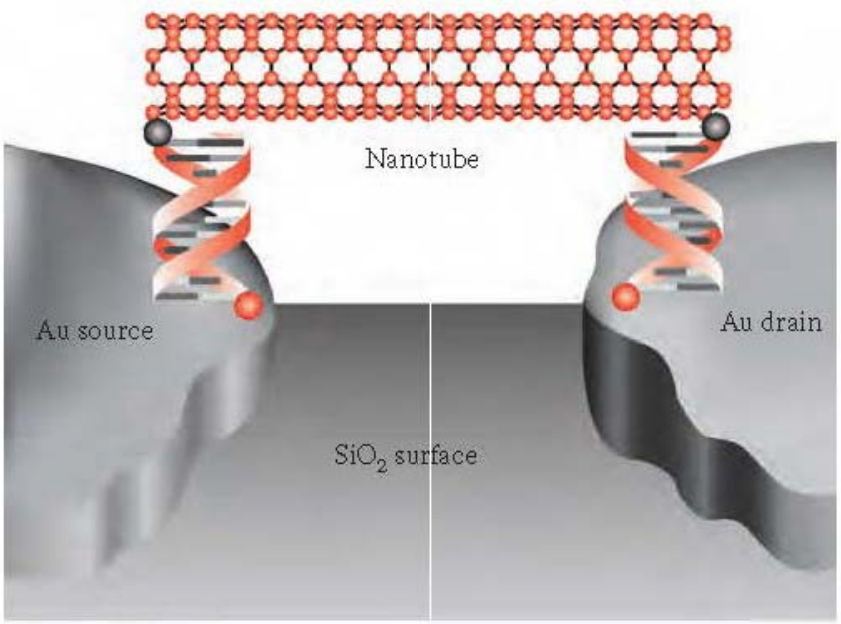

Figure 12.14 Illustration of DNA single helix attached to gold (Au) electrodes and the complementary base pairs of the other helix attached to ends of a nanotube. [Adapted from Hazani, M. et al., *Appl. Phys. Lett.*, 85, 5025, 2004; http://

12.10.3 DNA Origami

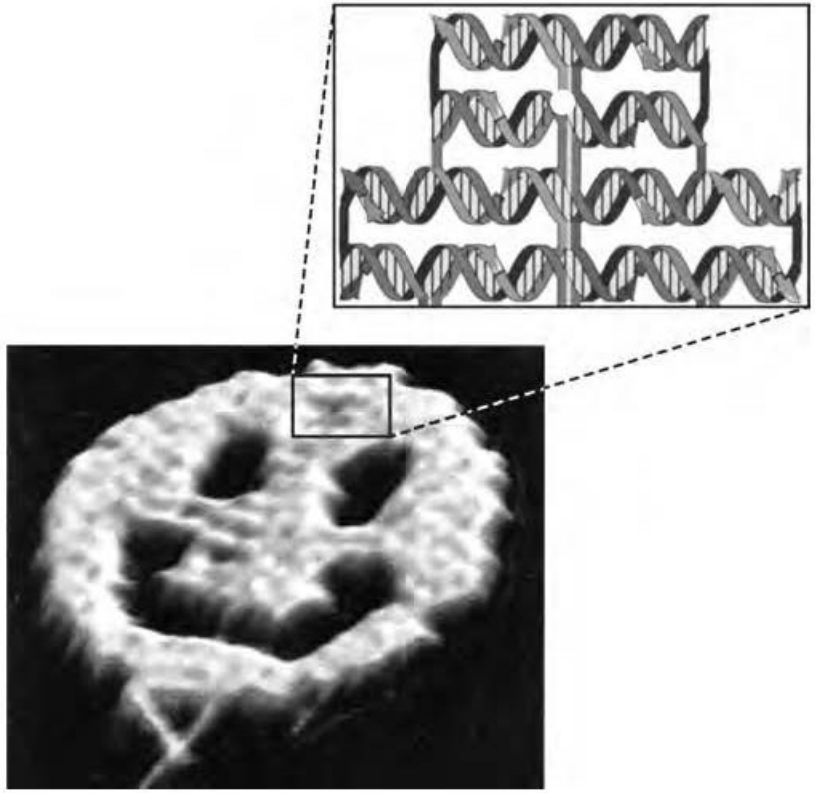

Figure 12.16 Self-assembled DNA origami of "smiley face" and an enlarged view of its structure. Single-stranded DNA is folded into a 2-D shape and stapled together with short DNA oligonucleotides. [Courtesy of Paul Rothemund,

12.11 Self-Assembled Monolayers (SAM)

- SAMs are defined as thin layers of molecules that deposit and bond to a substrate and change the surface tension of the substrate: head group, chain, and terminal group.

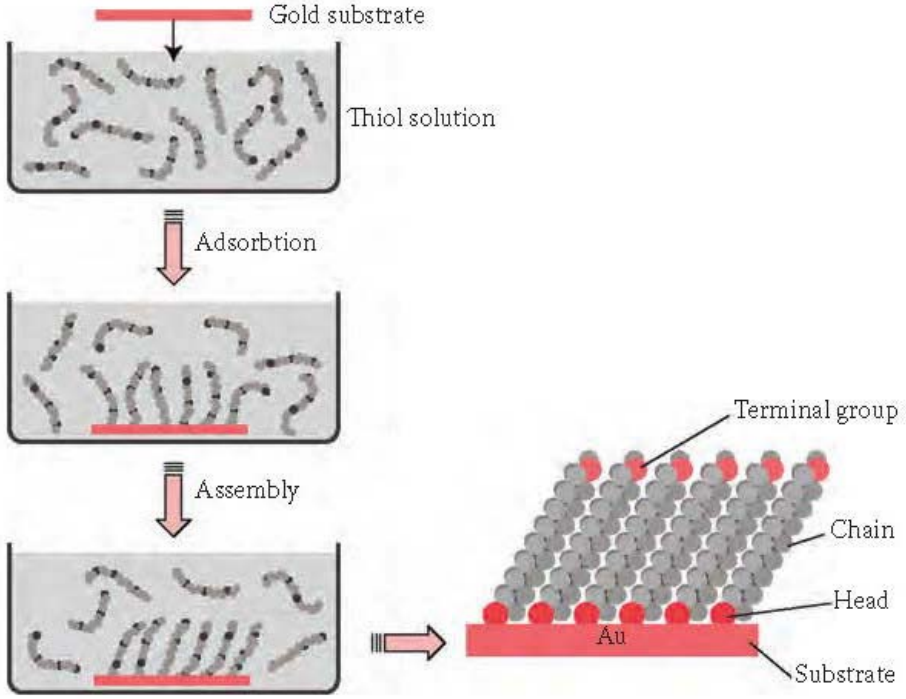

Figure 12.19 Illustration of Au substrate dipped into thiol–ethanol solution to form a SAM—molecular chain attached to gold substrate. [Adapted from Self-assembled monolayers, http://soft-matter.seas.harvard.edu/images/b/bc/Samsfig2.jpg