

Chapter 1

Age of Materials

When nature finishes to produce its own species, man begins using natural things in harmony with this very nature to create an infinity of species.

Leonardo da Vinci

Age of Materials

Human civilizations are often divided into ages according to the materials that dominate in the society. For example, in the Stone Age, when the tools were largely made of stones, people used those simple stone tools to improve their life style and advanced their civilization. In the Bronze Age, when most tools were made of bronze, so that a number of technological innovations were fostered and eventually altered the landscape of the civilization that made the Stone Age obsolete. Into the Iron Age, when the processing of iron was discovered and the society advanced tremendously. Many new tools were built, so that rapid and farther transportation becomes possible. People then explored many lands and seas, otherwise unreachable before.

We have entered the modern materials age, the “Plastic Age” in last half of the 20th century, the “Silicon Age” in the last quarter of the 20th century and continue to this day. These new materials have fundamentally transformed our life style forever and made a vast world into a globe village. What kinds of materials lie ahead in the future? It is believed that the “Designed Materials” through building from the bottom-up at the molecular scale combining all elements in predetermined manner, will likely play a key role in constructing and processing the future composite and integrated materials. This will be achieved both through discovering the nature’s designs that have been evolved from eons of selection, and through knowledge-based designs. These materials will again undoubtedly transform our civilization, as we know it today. These new materials will be the foundation for the future generations of “Designed Materials Age”.

The “Designed Materials Age” requires new knowledge to build advanced materials. It not only requires fully understand the individual building blocks, but also deep knowledge of the simple construction motifs. It is from simplicity to complexity.

Much like the constructions of the Pantheon of Athens, Forbidden City of Beijing, St. Peter's Cathedral of Rome, The Dome of Florence, the Tower of London and the Norte Dame of Paris, the "Designed Material Age" needs the basic building blocks and construction motifs. These building blocks and motifs are at the atomic and molecular scale. In the alphabet, 26 simple letters can be made into countless words that can in turn string into beautiful phrases, which can be used to construct into increasingly complex paragraphs, chapters and eventually, books and volumes of books.

In nature, through billions of years of prebiotic and molecular selection and evolution, there are bio-organic molecules, including 20 amino acids, few nucleotides, a dozen of lipid molecules and 2 dozens of sugars. There are also some naturally modified building blocks, or metabolic intermediates. Now hundreds of man-made derivatives have now been added to the list. These natural and synthetic building blocks, much like the 26 English alphabet letters with additions of foreign letters, are the key elements for the designed materials. The metals, composite of salts as well as other simple elements are complementary inorganic building blocks. When these bio-organic and inorganic building blocks are well coalesces together, either through molecular self-assembly or programmed assembly, to form stable structures with new functionality, a designed new material is born.

One of the approaches to design new materials is through molecular self-assembly. Molecular self-assembly is ubiquitous in nature. It has recently emerged as a new approach in chemical synthesis, nanotechnology, polymer science, materials and engineering. Molecular self-assembly systems lie at the interface of molecular and structural biology, protein science, chemistry, polymer science, materials science and engineering. Many self-assembling systems have been developed. These systems range from bi-, tri-block copolymers, and complex DNA structures, lipids, simple and complex peptides and proteins. Molecular self-assembly systems represent a significant advance in the molecular engineering of simple molecular building blocks useful for a wide range of applications.

The basis of self-assembly and molecular self-assembly

Self-assembly is ubiquitous in nature at all scales, from macroscopic to microscopic scales, from meters to nanometers. Assemblies of schools of fish in the ocean, flocks of birds in the sky, herds of wild animals on the plain are examples of such events. At the microscopic scale, oil droplets in water, assembly of DNA into double helix and ribosome that manufacture of proteins in the cell, are all belong to self-assembly. Self-assembly describes the spontaneous association of numerous individual entities into a coherent organization and well-defined structures to maximize the benefit of the individual without external instructions.

Molecular self-assembly is the spontaneous organization of molecules under thermodynamic equilibrium conditions into structurally well-defined and rather stable arrangements through a number of weak and noncovalent interactions. These molecules undergo self-association forming hierarchical structures. The key engineering principle for molecular self-assembly is to artfully design the molecular building blocks that are able to undergo spontaneously stepwise interactions and assemblies through the formations of numerous noncovalent weak chemical bonds. These typically include hydrogen bonds, ionic bonds, electrostatic interaction, van der Waals interaction, water-mediated interaction to assemble these molecules into some well-defined and stable hierarchical macroscopic structures. Although each of the bonds and interactions is rather weak, the collective interactions can result in very stable structures and materials. The key elements in molecular self-assembly are chemical complementarity and structural compatibility.

Like hands and gloves, both the size and the correct orientation, *i.e.* chirality, are critically important in order to have a complementary and compatible fitting. Chemical complementarity plays a key role in design new structures and materials. For example, the bases of adenine can form pairs with thymine, but not guanine and cytosine in a DNA double helix. The adenine and thymine form 2 chemically complementary hydrogen bonds with 10.8 Å distance between the C-1' linkage of ribose. Each member donates 1 hydrogen, and at the same time accepts 1 hydrogen. The structural fitting is also perfect. The same is true for guanine and cytosine pairing except they form 3 chemically complementary hydrogen bonds, where cytosine donates 2 hydrogens and accepts one; on the other hand, guanine donates 1 and accepts 2 hydrogens. The distance between their C-1' linkage of ribose is 11.1 Å. If the adenine is changed to guanine through mutations, such exposure to chemical agents, it can no longer pair with thymine, rather guanine pairs

with cytosine. Even though the pairing size remains about the same, they are not chemically complementary.

Structural compatibility is another key aspect of design. Two purines, adenine and guanine pairing will be too large to fit comfortably together into the double helix even they may form 2 hydrogen bonds. Likewise, two pyrimidines, thymine and cytosine, are too small to bridge the double helix to form the conventional hydrogen bonds. The structural compatibility aspect extends beyond the nucleic acids.

Molecular self-assembly in nature

Biomimicry and designing nature-inspired materials through molecular self-assembly is an emerging field in the 21st century. Nature is a grand master at designing chemically complementary and structurally compatible constituents for molecular self-assembly through eons of molecular selection and evolution. Chemical evolution from the first groups of primitive molecules through countless iterations of molecular self-assembly and disassembly has ultimately produced more and more complex molecular systems.

The constituents of biological origins, such as phospholipid molecules, amino acids and nucleotides have not been generally considered to be useful materials for traditional materials science and engineering. The advent of biotechnology and genetic engineering coupled with the recent advancement in chemistry of nucleic acids and peptide syntheses has resulted in a conceptual change. Several recent discoveries and rapid developments in biotechnology, however, have rekindled the field of biological materials engineering. In the last decade, considerable advances have been made in the use of peptides, phospholipid and DNA as building blocks to produce biological materials for a broad range of applications. Molecular self-assembly is emerging as a new route to produce novel materials and to complement other materials, *i.e.*, ceramics, metal and alloy, synthetic polymers and other composite materials.

There are ample examples of molecular self-assembly in nature. One of the well-known examples is the silk assembly. The monomeric silk fibroin protein is approximately 1 micrometer but a single silk worm can spin fibroins into silk materials over two kilometer in length, two billion times longer! Such a marvelous engineering

skill can only make us envy. Human ingenuity and current advanced technology is far behind the seemingly easy task by the silkworm. Likewise, spiders are grand master fiber engineers who can produce many types of spider silks through self-assembly the building blocks in a variety of ways, thus producing spider silk fibers with tremendous strength and flexibility. These building blocks are often at the nanometer scale. However, the resulting materials could be measured at meters and kilometer scales.

Likewise, the size of individual phospholipid molecules is approximately 2 nm in length, but they can self-assemble into millimeter size lipid tubules with defined helical twist, many million times larger. A number of applications have been developed.

The power of molecular self-assembly can never be underestimated. Molecular self-assembly can also build sophisticated structures and materials. For example, collagen and keratin can self-assemble into ligaments, and hair, respectively. In cells, many individual chaperone proteins assembly into a well-defined ring structure to sort out, fold and refold proteins. The same is true for other protein systems such as sea-shell biomineralization. Likewise, mammals build their teeth through self-assembly of a protein scaffold that is made of many individual proteins first and recruit calcium ions to the sites for biomineralization.

This book explores new ways to further advance “designed materials” from the bottom-up approach, using all knowledge we learned from nature and improved over the years of human ingenuity and creativity. Nature has inspired us at all levels, especially at the molecular scale, and we will move many steps farther.

Further readings

Strathern, P. (2000) *Mendeleev's Dream: the quest for the elements*. Penguin Books, London, UK

White, M. (2000) *Leonardo: the first scientist*. An Abacus book, Little, Brown & Co. London, UK

Feltwell, J. (1991) *The story of silk*. St. Martin's Press, London, UK



Fig. 0-1. The Great Wall of China. The Great Wall stretches to a total of 5,600 kilometers and was made with over 3 billion of individual bricks, each has a size of approximately 10 x 20 x 30 centimeter. This is a typical programmed assembly by human. If we can reduce the size of the building bricks 10-100 million times, in 1 x 2 x 3 nm, the size of an average protein, or 10 x 20 x 30 nm, an average protein complex, we would have entered a realm of nanoworld. DNA is almost like the nano-Great Wall. The wall with individual bases stretches over 2 meters long using 3.2 billion A, T, G, C bases in a single human skin cell.



Fig. 0-2. The San Simeon Piccolo dome in Venice, Italy. The dome is surrounded with scaffolds, each of the metal rods has a diameter approximately 4 cm, 500 time smaller than the size of the dome, which has a diameter approximately 20 meters. Each of the rods serves as the construction scaffold for building or repairing the dome that is truly enclosed in 3-dimensions. The scaffold is eventually removed. Many proteins and other

biological scaffolds have served to self-construct much large structures, such as shells, inorganic cages, bones and teeth, from the bottom-up.