Chapter 6
Self Assembly

6.1 Introduction

The term 'Self Assembly' itself indicates its meaning. It is a gathering or collection of certain entities without any external influence. Although the term 'self assembly' has received a scientific acceptance over the last 3–4 decades and such assemblies are recognized in biology, chemistry or physics, some philosophers like Kanad, Democritus and Descarates several centuries back had imagined that everything in the world, from small objects around us to solar system, galaxies and universe is a result of tiny, non-divisible units (or atoms). The word *ἄtomos* (Greek: ἄτομος) was first used by Democritus to mean uncuttable. Out of a chaotic situation, the various forms of matter get ordered following some laws of nature. Today we know that atoms can be further smashed with very high energy into still tinier particles viz. electrons, protons and neutrons. Protons and neutrons also are composed of fundamental particles like quarks. Yet, the concept that matter is composed of tiny units like atoms or molecules is still very useful for understanding most of the phenomena around us.

One may tend to think that the term 'self assembly' can be used for any matter in which atoms or molecules stick together, like in a solid. However this is not the case. As will be discussed in this chapter the term self assembly applies for spontaneously formed, reversible, locally ordered, thermodynamically stable assemblies. Self assemblies are very sensitive and can transform back to the state of disorder. In disorder state there are some building blocks or motifs which are uniform in the shape and size which assemble to form ordered structure by some weak interactions spontaneously. The building blocks themselves is an assemblage of strong interacting particles (atoms or molecules).

Self assembly initially, during the twentieth century, was considered to be limited to biological world where origin of beautiful colours of peacock feathers,

S.K. Kulkarni, *Nanotechnology: Principles and Practices*,
DOI 10.1007/978-3-319-09171-6_6

butterfly wings and many birds or insects were understood as a result of ordered structures. Microscopy analysis reveals that often there are micro plus nano or just nanostructures involved. Phenomenon of self assembly occurs at many length scales and is not only limited to tiny objects but even gigantic astronomical objects like stars, planets, galaxies and entire universe which have been considered as a kind of self assembly.

Observations of self assembly in naturally occurring living and non-living world have led scientists to understand what leads to the ordered or random assemblies of some smaller entities, blocks, motifs or units. We know that the major bonds prevailing in the inorganic solids are ionic, covalent or metallic. They have rather large energies of formation (or dissociation) typically from $\sim$0.5 to a few electron volts. Self assemblies are formed spontaneously by weak interactions like π-π, van der Waals, colloidal, electrical, optical, shear or capillary forces.

In nanotechnology, self assembly plays an important role. Close packed arrangement of organic molecules and nanoparticles is useful in novel devices. The technique of organic thin films deposition by Langmuir-Blodgett (L-B) technique discussed in Chap. 4 (Sect. 4.6) is a very nice example of self assembly. However, there was no specific recognition of the term 'self assembly' associated with L-B technique. The term 'self assembly' became popular when Nuzzo and Allara in 1983 used this terminology when some disulphide alkyl molecules were deposited on gold surfaces.

Recognition of importance of self assembly and its origin has led scientists to make deliberate attempts to fabricate self assembled organic, inorganic or materials useful to obtain novel, electrical, mechanical, magnetic or optical materials with unprecedental properties. Langmuir-Blodgett films, micelles, liquid crystals, layers obtained by dip-pen lithography, deposition of materials in the voids of the self assembled spheres, and anodization of alumina templates with ordered pores are some of the methods to realize self assembled structures with desired materials. Such structures are useful to create photonic band gap materials, novel sensors, lasers, Bragg mirrors, electroluminescent devices, photovoltaic solar cells to name a few. Nanofabrications using DNA have potential applications in nanoelectronics, nanomechanical devices as well as computers.

A very important branch developed in chemistry, known as "Supramolecular chemistry" is solely the manifestation of 'self assembly'. The term "Supramolecular chemistry" was coined by Nobel laureate Jean-Marie Lehn to mean the *chemistry beyond molecules*. It is essentially an assemblage of molecules of one or few more types to make aggregates or larger crystals through non-covalent interactions. The 'molecular recognition' (like lock and key) helps build larger assemblies as in two strands of DNA winding around each other. Three dimensional ordered arrangement of such molecular assemblies can lead to build up 'superlattices' or large single crystals of self assembled molecules.

6.2 Mechanism of Self Assembly

It is important to realize that the self assembly involves weak to strong forces and nanoscopic to gigantic structures in one, two or three dimensions. As mentioned in the introduction, the self assembly can be a result of very weak forces like van der Waals interaction, hydrogen bonds, static charges, magnetic interactions and so on. The driving force behind the self assembly has been recognized as due to attempt of any system to go to the lowest energy state. Ability of a system to go to a well ordered low energy state depends upon the availability of units of same size and shape. Molecules with definite shape, number of atoms and therefore size, already in the state of low energy are good candidates for the self assembly. It should be remembered that atoms in such molecules or building blocks of self assembly themselves are held together by stronger forces.

When the building blocks (one, two or more types of building blocks also can form self assemblies) are available for self assembly, state of minimum energy may be attained spontaneously in the absence of any external force. However self assembly may occur in the presence of an external driving force like temperature, pressure, magnetic field and so on. These two types viz. assembly in the absence and presence of an external driving force are known as *static* and *dynamic* assemblies respectively (see Fig. 6.1). Static assembly is realized when system achieves minimum energy state and can stay there unless it is subjected to strong external forces. On the other hand, dynamic self assembly involves constant influence of external force from the ambient. If the energy intake from the ambient stops, the self assembly can leave the state of organized structure and de-assemble. Formation of ordered crystalline structure from a melt can be considered as an example of static self assembly. Thin films formed by L-B technique (Chap. 4) or dip pen lithography

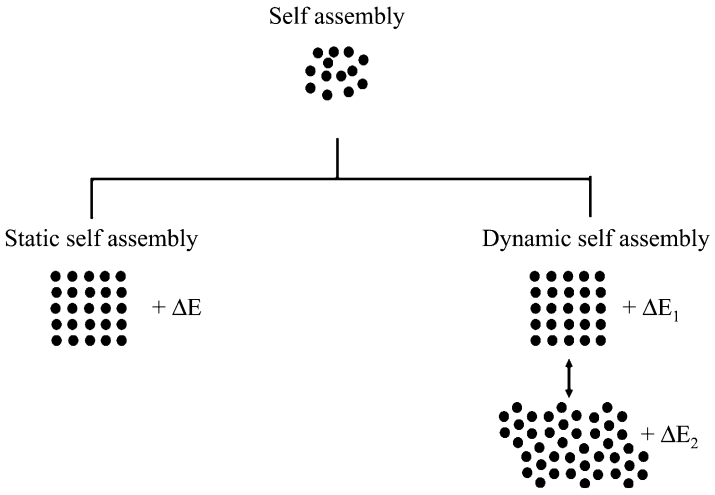

Fig. 6.1 Two types of self assemblies

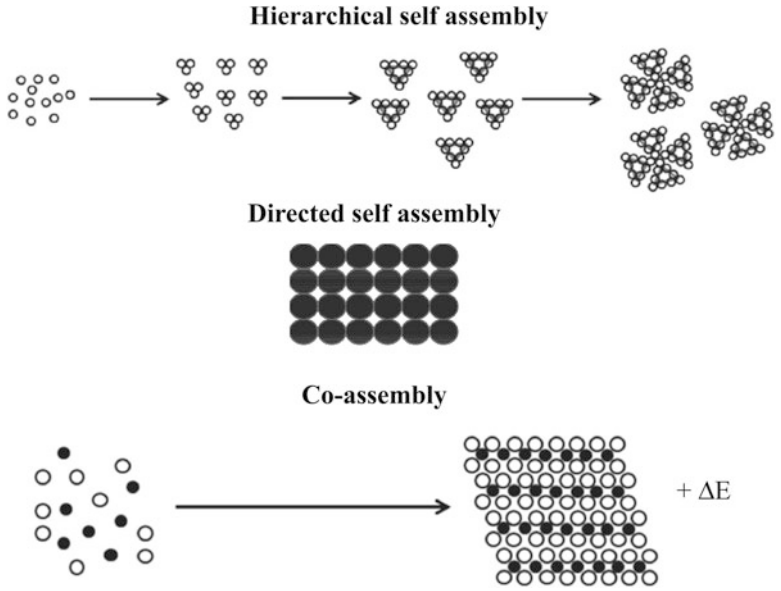

Fig. 6.2 Hierarchical and co-assembly

technique (to be discussed in Chap. 9) also are examples of static self assembly. The living animals or plants form good examples of dynamic self assembly. As soon as the supply of food, proper temperature and air pressure discontinue, the animals and plants disintegrate.

The static and dynamic assemblies can be further divided into '*hierarchical self assembly', directed self assembly*' and '*co-assembly'* as illustrated schematically in Fig. 6.2.

Hierarchical self assembly is characterized by small range, medium range and long range interactions of one type of a building block.

Directed self assembly occurs when the building blocks occupy the pre-designed places like some portions of a lithographically patterned substrate, pores in membranes or spaces between ordered particles.

Co-assembly, as the name suggests, can be formed with two or more types of blocks which can fit into each other.

We shall discuss in the following section some examples of self assembly. Evaporation or biological templates like DNA or S-layers are useful for self assembly. In most of these cases, it is possible to place the nanoparticles at some well determined location of polymer chain, organic molecule or template through specific bonding. When well structured templates like S-layers or DNA are used, direct patterning of nanoparticles becomes feasible. These are the examples of inorganic (nanoparticles)-organic molecules or inorganic-biomolecules assemblies. However it is also possible to have assemblies of purely inorganic particles. The driving force for such assemblies is often quite different. We shall discuss now little more details of various assemblies.

6.3 Some Examples of Self Assembly

6.3.1 Self Assembly of Nanoparticles Using Organic Molecules

Preformed inorganic nanoparticles can be assembled on solid substrates through some organic molecules adsorbed on their surfaces. For example CdS nanoparticles functionalized with carboxylic (-COO^-) group can be transferred (Fig. 6.3a) to aluminium thin films. Dithiols adsorbed on metal surfaces also could adsorb CdS nanoparticles (Fig. 6.3b) to form layers of them. Silver particles (Fig. 6.3c) have been adsorbed on oxidized aluminium layers using bi-functional molecule such as 4-aluminium layers carboxylthiophenol. Molecules bind to aluminium oxide layer through carboxylic group and thiol attaches to silver particles.

Using a two-phase reaction alkanethiol or alkylamine capped gold, silver, palladium etc. nanoparticles have been self assembled. Here chemical reaction takes place in an aqueous medium. The particles are then transferred into an organic solvent and drop casted on an appropriate solid substrate. Solvent is allowed to evaporate which leaves self assembled layer.

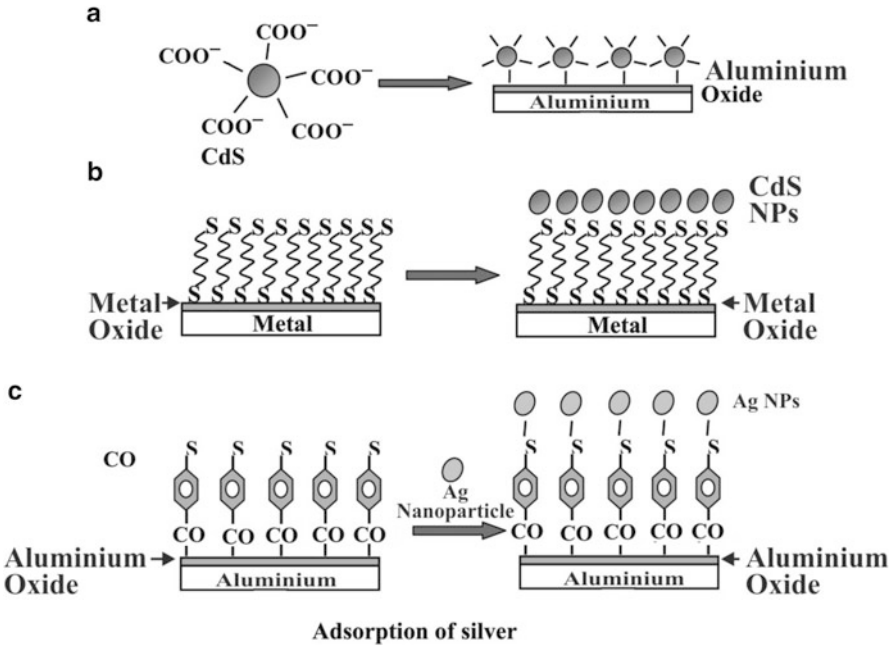

Fig. 6.3 Self assembly of nanoparticles

6.3.2 Self Assembly in Biological Systems

There are many examples of self assembly in the biological systems like S-layers, proteins or DNA. When organized arrays of inorganic crystals are embedded in biological systems they are often referred to as biomineralized systems. Here we shall discuss only the ordered self assembled layers as examples of biomineralization.

Magnetotactic bacteria are small bacteria, ∼35–120 nm sized with permanent magnets inside them. The magnets are of either iron sulphide (Fe_3S_4-greigite) or iron oxide (Fe_3O_4-magnetite). Such magnets make a chain of nanomagnets. The size 35–120 nm is quite critical and smaller or bigger magnets would not have served the purpose for which these magnets are used. The magnets smaller than 35 nm cannot have permanent magnetism at ambient temperature and those larger than 120 nm would have reduced magnetism due to multidomain formation above this size. Only those between 35 and 120 nm size are single domain permanent magnets, the chain of which is useful for navigation of bacteria. These bacteria live in mud, marshy areas, ponds or sea. and prefer anaerobic condition. If by any chance they come to the surface of water or soil, they navigate downwards making use of their magnets aligning in the earth's magnetic field direction. Earth's magnetic field has a dip in the north and south hemispheres which helps bacteria to seek downwards direction. Even some birds have ordered nanomagnets which they sometimes use for navigation purpose.

A very common self assembly in biological systems is S-layers. They are one of the simplest kind of biomembrane evolved during billions of years and is invariably a part of cell envelope of prokaryotic organisms, with just a few exceptions. They are two dimensional, crystalline single proteins or glycoprotein monomers organized in hexagonal, oblique or square lattices, as illustrated schematically in Fig. 6.4.

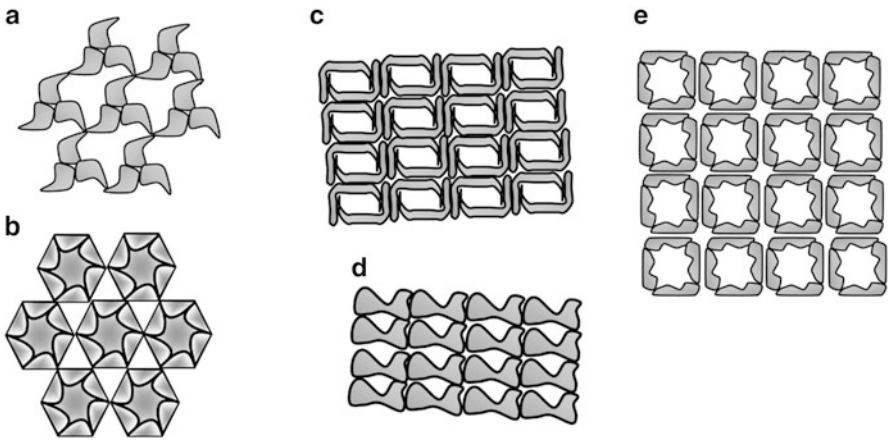

Fig. 6.4 Different types of S-layer lattice

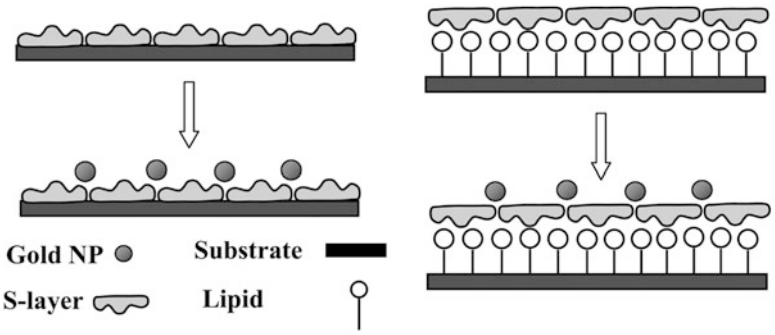

Fig. 6.5 Assembly of CdS nanoparticles using S-layer

These lattices have ordered pores. The periodicity of pores can vary, depending upon the protein, from 3 to 35 nm. In some cases pores ∼2–8 nm have also been observed.

Such S-layers after extraction from bacterial cells have been transferred on some metallic substrates (or grids). When treated with cadmium salt and subsequently with Na_2S, ordered arrays of CdS nanoparticles could be formed. This is confirmed using electron microscopy. S-layers are reported to have been used to assemble Au, Pt, Fe and Ni metal nanoparticles. In general, S-layers extracted from the biological cells can be directly used to deposit nanoparticles from liquid or vapour phase as shown in Fig. 6.5.

It was discussed in Chap. 5 that ferritins are protein colloids of 12 nm size found in all animals. Ferritins have cavities ∼6–8 nm in size filled with iron oxide. It is possible to remove iron oxide and replace it with metal or other nanoparticles. Further it is possible to make a two dimensional array of ferritins in solution. For example ferritin solution in NaCl and phosphate at ∼5.8 pH can be filled in a trough. Chloroform containing dichloroacetic acid can be used to dissolve poly-1-benzal-L-histidine (PBLH) and spread over ferritin solution in the trough. After about two hours the solution can be heated at 38 °C for one hour and cooled back to room temperature. This produces ordered layer of ferritin at liquid-air interface. The layer can be transferred on silicon substrate by dipping it in the solution. An ordered layer of ferritins is transferred on the surface. By heating the silicon substrate for one hour in nitrogen ambient at 500 °C, protein from ferritin is completely removed, leaving an ordered layer of iron oxide or whatever nanoparticles were filled in ferritin. There are several reports of two dimensional ordered layers being transferred by this route of Co, CoPt, FePt. The major application of this type of layers is in high density magnetic data storage systems. It is speculated that CoPt particles in this manner will be able to have as large as 1,550 Gbit/cm^2 per particle. This is quite large compared to current ∼11 Gbit/cm^2.

DNA (deoxyribonucleic acid) is a long helical molecule and was discussed in Chap. 5. It has a large aspect ratio (i.e. ratio of length to diameter is large) and acts like a long one dimensional template in its simplest form. Its four nucleotide bases

viz. quinine (Q), cytosine (C), adenine (A) and thymine (T) can form a rich variety of sequences and structures. Thus circular, square, branched and many more long (few micrometre) or short (few nanometre) DNA templates are possible. Besides planer geometry, they can adopt even three dimensional structures. As DNA has alternate sugar and phosphate groups on its strands, it is possible to anchor metal, semiconductor or oxide particles by different bonding on DNA to have assembly of particles.

6.3.3 Self Assembly in Inorganic Materials

It is possible to spontaneously create the quantum dots for example of germanium (Ge) on silicon (Si) or indium arsenide (InAs) on gallium aresenide (GaAs). The origin of self assembly is strain induced. Germanium and silicon have only 4 % lattice mismatch. Therefore Ge can be deposited epitaxially on Si single crystal upto 3–4 monolayers. Although grown (hetero)epitaxially, the layers of deposited Ge are highly strained (coherently i.e. without any defects or dislocations). When further deposition takes place, the lattice strain caused by depositing Ge on Si with different lattice constants cannot be accommodated.

This results in spontaneous formation of nanosized islands or quantum dots. However the temperature of the substrate has to be >350 °C during deposition or post-deposition annealing is required. Figure 6.6 schematically illustrates the growth mechanism as well as an electron microscopy image of germanium islands on Si (111) surface. The size of the islands depends upon the growth temperature as well as the substrate plane on which it grows.

Preformed inorganic particles of materials like silica (SiO_2), titania (TiO_2), polymer beads or latexes are able to organize themselves just by sedimentation also. But they need to have very uniform size. As illustrated in Fig. 6.7, organization of SiO_2 particles is quite clear. The silica particles can be formed by a sol-gel route. The particles synthesized in aqueous medium are simply allowed to evaporate from

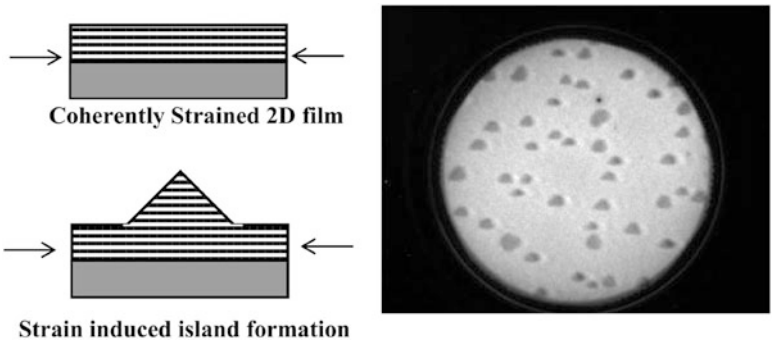

Fig. 6.6 Growth mechanism of Ge on Si and photograph showing island formation (Field of view 10 μm)

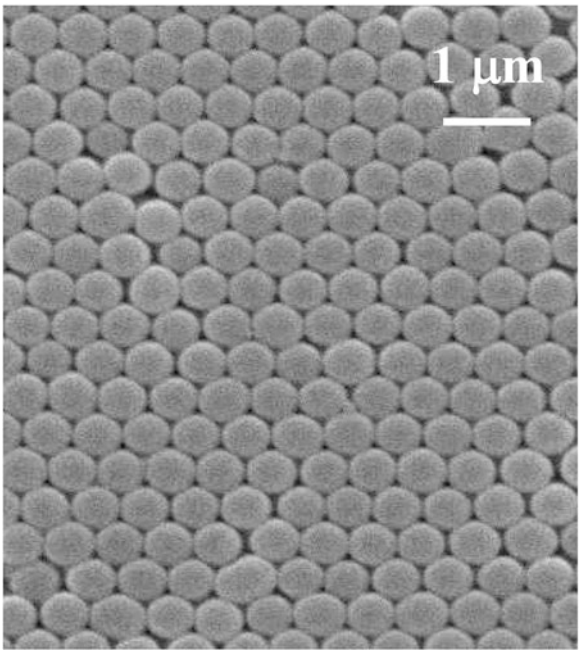

Fig. 6.7 SEM image of self assembled silica (SiO_2 particles) on glass slide

the solution drop placed on a glass substrate. After some time the particles self assemble due to weak van der Waals interaction amongst the particles. The driving force is the capillary force. Minimization of surface energy takes place by forming a hexagonal network. The uniform size of the particles is helpful to make an ordered two dimensional network of particles.

Self assembly thus has a very rich variety of practical examples. Many other self assemblies can also be designed and fabricated. Such assemblies have a great potential in molecular information technology as it is possible to store information and process information. It also is useful for nanofabrication. If complex arrangements of self assembly can be made like in biological processes, compact devices can also be realized using self assembly. One such example given by Lehn is the brain which is self assembled and wired by self organization to different organs. It is able to store information, process and also has control over different body parts, all through self assembly or organization.

Further Reading

H. Dodziuk, *Introduction to Supramolecular Chemistry* (Springer, Dordrecht, 2002)
J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives* (VCH, Weinheim, 1995)
Materials Today, special issue on Nanofabrication by Self Assembly, **12**, May 2009
J.W. Steed, D.R. Turner, K.J. Wallace, *Core Concepts in Supramolecular Chemistry and Nanochemistry* (Wiley, New York, 2007)