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## Chapter

# Introductory Chapter: Self-Assembly of Nanostructures

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## 1. Introduction

Self-assembly is a process by which building blocks are put together in a parallel fashion without external stimuli. The structures and patterns that emerge from the self-assembly can be small or large, depending on the interaction forces between the building blocks and their kinetic pathways during the self-assembly. Self-assembly dates back to 400 BC, when Democritus, a Greek philosopher, envisioned that the earth and solar system might have evolved from organization of atomistic components [1]. Later, Descartes, a French philosopher, postulated that the universe has self-structured out of chaos via organization of small components to large assemblages according to natural laws of physics [1]. In 1935, Langmuir and Blodgett developed a method to form a closely packed monolayer of amphiphilic molecules on solid and liquid surfaces [2]. In 1946, Bigelow observed the assembly of a monolayer of long alkylamine chains on a solid surface. Although these studies did not use the term “self-assembly”, they were indirectly explaining the self-assembly process. The self-assembly was initially used in Self-assembled monolayers (SAMs), which were discovered in 1983, when Nuzzo et al. developed well-ordered monolayers of alkanethiolate molecules chemisorbed on gold surfaces [3–5].

Aforementioned ideas, observations, and discovery have led to the current thinking of fabricating nanostructures via self-assembly, which is spontaneous organization of ordered structures from disordered phase of nanoscale constituents in the absence of external stimuli. Self-assembly manifests a bottom-up approach in nanofabrication, and enables an efficient way to create functional materials from nanoscale building blocks. Current nanotechnology utilizes two approaches for nanomanufacturing: (i) top-down approach, where materials are manipulated at the macroscopic scales in serial steps to fabricate functional construct at the nanoscale, and (ii) bottom-up approach, where materials are constructed by assembly of nanoscale building blocks to form functional construct at macroscopic scales.

Controlling the size, shape, and surface properties of the building blocks determines how ordered the organization of constructs in the self-assembly will be. As such, synthesizing the nanoscale building blocks with desired shape, size, and properties is the primary goal in the self-assembly. In addition, with specific properties of the building blocks, e.g. charge, binding affinity, and hydrophobicity/hydrophilicity, one will be able to control the interaction forces between the building blocks, and their kinetic pathways during the self-assembly. These interaction forces can span multiple length scales. In the absence of external stimuli, the self-assembled configuration is settled by overall energy minimization of the system. This self-assembled structure will be static, and correspond to a local minimum energy configuration, which may be kinetically trapped. However, in the presence of external stimuli,

the self-assembled configuration will correspond to a local energetic minimum, which depends on the influx of energy from the external stimuli. As soon as the external stimuli cease to exist, the energetic minimum will disappear, and the assembled configuration will dismantle.

## **2. “Hierarchical” and “directed” self-assembly**

Self-assembly process can be done in various ways among which “hierarchical” and “directed” self-assembly are very common in nanofabrication. In hierarchical self-assembly, structuration of the building blocks occurs over multiple length scales. Initially, at the smallest length scale, self-assembly of the original building blocks takes place. The assemblages that grow out of the first level of assembly form the building blocks for the second stage. This hierarchy of self-assembled building blocks continues at multiple levels, which span multiple length scales. An example of hierarchical self-assembly is the mesostructure of Siloxane-organic hybrid films with ordered macropores [6]. These hybrid films have spanned three length scales during self-assembly, (i) microscopic length scale at which assembly of tetrahedral silica blocks in the presence of polystyrene particle template takes place, (ii) mesoscopic length scale at which ordered mesoscopic pores form, and (iii) macroscopic length scale at which macroscopic air voids with silica intercalated network is assembled.

In contrast to hierarchical self-assembly, in the directed self-assembly an external stimulus is used to drive the assembly in a desired direction. One way to direct the self-assembly is to provide a lithographic template, and use the template to guide colloidal particles or nanoparticles in a solution to self-assemble on the template surface [7]. One example of directed self-assembly is the dip-pen nanolithography, whereby AFM tip and water meniscus is utilized to direct chemical reagents to form a SAM on nanoscopic areas of the target surface [8]. Directed self-assembly can further be divided to static and dynamic self-assembly. In static self-assembly, the external forces drive the system to an equilibrium state. The system dissipates energy as it moves towards a static equilibrium. At this equilibrium, the self-assembled structure will retain its configuration there after even if the external stimuli are removed; hence called static self-assembly. In contrast, dynamic self-assembly generates stable assemblages, which may not be at thermodynamic equilibrium. These stable configurations persist as long as the external stimuli are present and the system dissipates energy [9]. These configurations can also be manipulated by rectifying the external forces. As soon as external forces are removed, the system will disassemble, and return to a thermodynamic equilibrium. An example of dynamic self-assembly is the self-organization of rotating magnetic disks floating at liquid-air interface in the presence of an external magnetic force, which attracts the disks towards the axis of rotation. As disks move at the interface, they create vortices, which repel the disks away from another. The balance between the attractive and repulsive forces gives rise to the dynamic self-assembled structure of the magnetic disks [10].

## **3. Conclusion**

Aforementioned applications are only a short list among many others, which suggest that self-assembly is a promising bottom-up approach that can potentially lead to a scalable and efficient nanofabrication technique. Nanofabrication of most of complex three-dimensional structures [11], functional materials [12],

nanocrystal superlattices that would look like nanorods, and inverse opals [6], or manufacturing nanowires with diameters less than 2 nm [13] have been reported by means of self-assembly; however, fabrication of these structures will pose a challenge, and be costly by top-down approaches. On the other hand, despite the advantages of self-assembly, and its promising potentials in nanofabrication, there are still challenges to utilize it for certain applications. These challenging applications include but not limited to:

(1) Designing semiconductors for inexpensive light harvesting systems with high power conversion efficiency, and enhanced thermal stability, (2) fabricating superlattices of quantum dot semiconductors with highly efficient refrigeration and power generation cycles for thermoelectric materials, (3) synthesizing solid-state light weight nanomaterials for lithium batteries with high energy density, and fast charge-discharge cycles, (4) positioning of nanoparticles with single particle resolution and sub-10 nm precision for nanoscale electronics, (5) synthesizing nanomaterials with highly selective electrocatalytic activities, (6) developing nanomaterials for carbon sequestration, and efficient conversion, (7) developing porous structures for fast hydrogen storage at atmospheric pressure, room temperature, and reversible usage, (8) developing a low cost, portable, rapid, and sensitive disease diagnostic sensors, (9) designing new drug delivery agents for treatment of targeted cancer cells, and (10) fabricating nanomotors with speed and direction controllability for payload delivery in biomedical applications.



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