

# SELF-ASSEMBLING NANOSTRUCTURES\*

# 10

## 10.1 INTRODUCTION

### 10.1.1 NANOTECHNOLOGY: DEFINITION AND BACKGROUND

Nanotechnology is the term used to cover the control, design, and understanding of functional materials or structures on an atomic or molecular scale. The field of nanotechnology draws on principles from nanoscale science, engineering, and technology to further understand fundamental physical and chemical properties of materials and structures at the nanoscale. It has been proven that nanoscale matter does not necessarily exhibit the same properties observed at larger scales. In fact, much of the awe around nanoscale matter can be attributed to how physical, chemical, and biological properties, phenomena, and processes are substantially improved as compared to the same matter at the macroscale. The improved properties exhibited by materials at the nanoscale can be attributed to the distinctive structural features of a given material existing as an intermediate in size between isolated atoms and bulk macroscopic materials. In the range that defines the scale of nanotechnology between 1 and 100 nm, a material may exist in a different form of state or display different physical characteristics from those of the same material on a larger scale (Kelsall et al., 2005). Improved particle and material characteristics at the nanoscale will enable for the creation of advanced applications and may also lead to potential challenges.

Although nanotechnology as a subject exists primarily on a research basis, there continues to be a steady incline in the transition from a theoretical approach to practical applications of nanotechnology. However, before nanotechnology can fully revolutionize industry and technology, there needs to be greater fundamental scientific understanding and technological expertise to comprehend how these nanoscale particles or molecules function. More specifically, a better understanding of how nanomaterials organize and assemble themselves, how they are constructed, and how they operate in complex nanostructured systems needs is essential to develop the field of nanotechnology. This chapter will discuss the theory behind one approach to organize and assemble nanoscale particles or molecules: the self-assembly of nanostructured molecular materials and devices.

### 10.1.2 SELF-ASSEMBLY: DEFINITION AND BACKGROUND

Self-assembly of constituent molecules on the nanoscale order has existed in nature as soft materials assemble to produce cell membranes, biopolymer fibers, and viruses (Kelsall et al., 2005). Recently

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in laboratories, scientists and engineers have been able to fabricate nanoscale materials through a bottom–up approach known as self-assembly. Self-assembly is a process in which particles or materials at the nanoscale spontaneously arrange predefined components into ordered superstructures which can be exploited in various applications. Fabrication of nanostructures can take place in a stirred vessel either by static or dynamic self-assembly. Static self-assembly is more common between the two and involves systems at equilibrium conditions that do not dissipate energy. Formation of a structure by static self-assembly requires induced thermal effects on the system but the product is stable, whereas dynamic self-assembly takes place when the system dissipates energy (Kelsall et al., 2005). Further discussion behind the principles of self-assembly will be highlighted later in this chapter.

### 10.1.3 IMPORTANCE OF SELF-ASSEMBLY

Many scientists consider self-assembly to be the most promising and simple method to incorporate nanoparticles into functional structures (Yang, Gu, Li, Zheng, & Li, 2010). The ability to easily control self-assembly based on organic materials allows the manufacturer to specialize electronic, magnetic, or photonic properties of inorganic components to achieve advanced functionalities from materials that may be nonexistent, difficult to extract, or have a limited source in nature. Fabricated nanostructures possess advanced properties that may be applied usefully in various potential applications, and these advanced properties of nanostructures have attracted interest from various fields of industry including biomedicine, computers, electronics, robotics, telecommunications, transportation, and water treatment, just to name a few. In [Section 10.5](#), articles have been reviewed to include specified applications for use in lithium-ion (Li-ion) batteries, supercapacitors, hydrogels, coagulants, optical filters, and visual displays.

Aside from the ability to formulate advanced properties of materials for specialized applications, the self-assembly fabrication method is considered to be the most feasible of the bottom–up approaches. Fabrication of self-assembled nanostructures in a stirred vessel is much more practical than other bottom–up nanostructure fabrication methods such as the arrangement of nanoparticles by hand or by a scanning tunneling microscope. In addition, various nanostructures of different morphologies can be produced through self-assembly by less effort (e.g., fewer hours of labor), lower cost (e.g., less material wasted and no need for expensive vacuum equipment), and in larger quantities than through top–down fabrication methods (Wang & Gates, 2009).

Although self-assembly has indicated promising results, industries are continuously investing into research and development to better understand the process of self-assembly to one day be able to implement it on a large-scale basis. Once self-assembly is fully understood, industries are hopeful to implement self-assembly for mass production of smaller, cheaper, faster, and overall better products. Complete understanding of nanotechnology and implementation of self-assembly and other fabrication methods may revolutionize the world as it is today.

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## 10.2 BUILDING BLOCKS

Common applications of soft materials are found in soaps, plastics, and paints. The process of self-assembling materials at the nanoscale follows a bottom–up approach—molecules are capable of assembling themselves into given superstructures. In nanotechnology, soft matter can be manipulated

by thermal stresses, thermal fluctuations, and chemical treatment to produce self-organizing soft materials such as liquids, polymers, and colloids to name a few. Self-organization of soft materials is also observed in nature through the development of cell membranes, biopolymer fibers, and viruses for example (Kelsall et al., 2005).

The self-assembly of amphiphiles, colloids, and polymers into mesophases influences the properties of soft materials and will be discussed as the building blocks in the formation of such materials. Soft materials can be divided into two categories: synthetic and biological. Synthetic, self-organizing soft materials are synthesized by mankind, whereas biological soft materials occur naturally and self-assemble by nature (Kelsall et al., 2005).

### 10.2.1 SYNTHETIC

The major building blocks of synthetic soft materials in current development at the nanoscale include the following: polymers, surfactants, lipids, colloids, and liquid crystals. Synthetic polymers can be made by a range of polymerization methods and techniques.

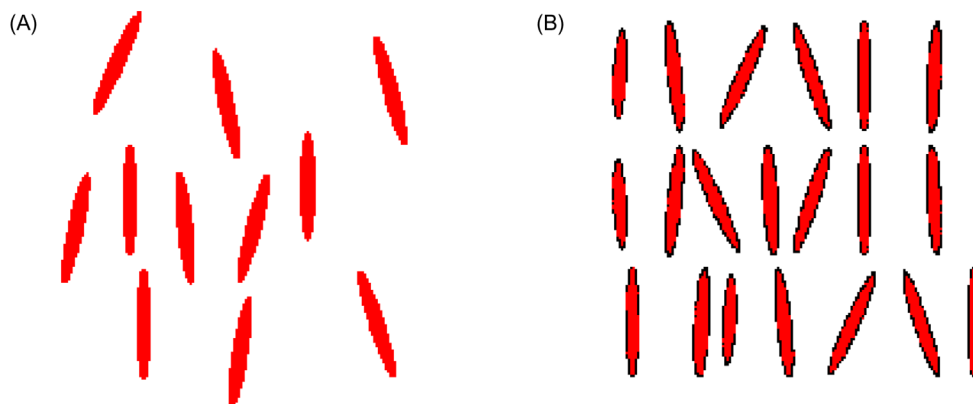
Conventional polymers spontaneously self-assemble into nanostructures (e.g., crystal lamellae in crystalline polymers). On the other hand, studies have been done in engineered self-assembly of polymers into designed structures, for example, microphase separation of block copolymers into nanostructures that become significant components in nanotechnology development (Kelsall et al., 2005).

Surfactants, which are surface-active agents, are made up of amphiphilic molecules containing hydrophilic tails and hydrophobic heads. On surfaces, the amphiphiles preferentially segregate and become active. An example of a surfactant is detergent. Another similar self-assembling building block is lipids which are biological amphiphiles. In water, lipids collectively gather together or aggregate into nanostructures to reduce the contact of the hydrophobic part of the amphiphiles with water molecules. Examples of nanostructures that are formed are micelles and vesicles. Micelles can be spherical or cylindrical and form hydrophobic cores and hydrophilic coronas in water. Vesicles are hollow spheres in which the outer surface is composed of layers of surfactant molecules (Kelsall et al., 2005).

Colloids are described as a microscopic substance dispersed evenly throughout another substance with dimensions in the range of 1 nm to 1  $\mu\text{m}$ . Colloidal systems are heterogeneous in nature and are composed of two separate phases. Self-organization of molecules occurs when the dispersed phase comes into contact and mixes with a continuous medium. Common examples of colloids include aerosols, foams, and emulsions (Kelsall et al., 2005).

The final synthetic, self-organizing soft material that will be discussed is liquid crystals. Liquid crystals are composed of moderate size organic molecules with molecular order intermediate between that of a liquid and of a crystal. Liquid crystals can form into two different phases—thermotropic and lyotropic liquid crystal phases which are also termed as mesogens. Thermotropic phases are formed by organic molecules in the absence of solvent, whereas lyotropic phases are formed by amphiphiles in a solution. Fig. 10.1 shows common orientations of liquid crystal phases (Kelsall et al., 2005).

In the nematic phase, the positional order of the molecules is short range, oriented in an average direction as shown in Fig. 10.1A. In the smectic (layered) phase, the molecules are oriented in long-range translational order illustrated in Fig. 10.1B. This smectic phase has a high viscosity and is generally not useful for devices (Case Liquid Crystal Group, 2010). Self-assembly of liquid crystal phases is an important component in cell membranes and electronic displays (Kelsall et al., 2005).

**FIGURE 10.1**

(A) Nematic phase and (B) smectic phase.

*From Liquid Crystal Primer, Case Liquid Crystal and Complex Fluids Group, 2010.*

## 10.2.2 BIOLOGICAL

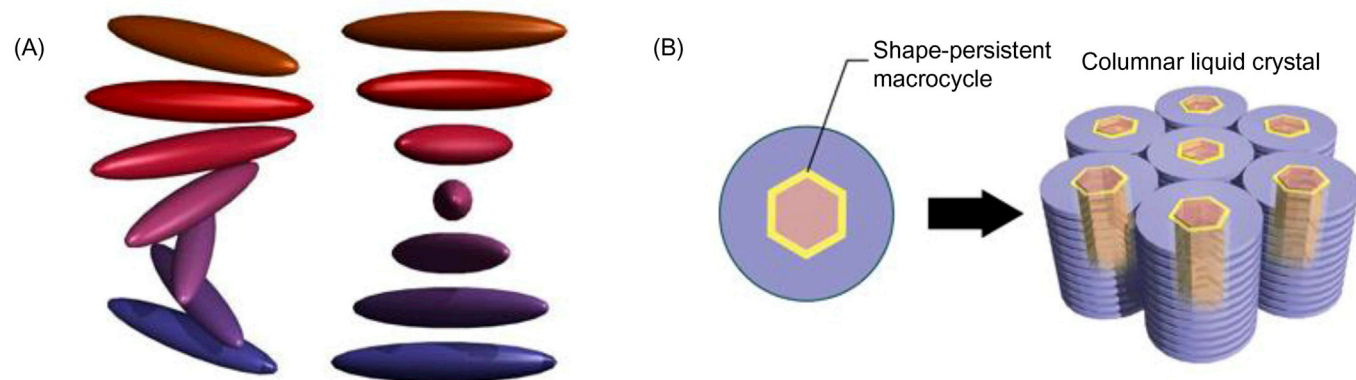
Self-organization of soft materials also occurs naturally, as opposed to being synthesized, which is therefore convenient and advantageous. Examples of biological self-assembling materials are silk, collagen, proteins, DNA, microtubules, and viruses. Each will be discussed with current applications in nanotechnology developments.

The structure of silk consists of antiparallel  $\beta$ -sheets of protein fibroin, in which  $\beta$ -sheets are formed by intermolecular hydrogen bonding between peptide chains. The orientation of polypeptide chains along the  $\beta$ -sheets is responsible for the tensile strength of silk whereas weak forces in between the sheets allow for the flexibility of the material. Insects and arachnids produce silk to build webs, nests, and cocoons. Silkworm cocoons in particular have been used by mankind to produce high-quality fabrics (Kelsall et al., 2005).

Another self-organizing soft material is collagen which is made up of proteins that are naturally formed in living species. The structure of this material takes the form of cross-linked fibrils or may undergo denaturation by heat or chemical treatment to produce gelatine. It is a major component of connective tissues in animals. Similarly, keratin is also comprised of fibrous proteins that form hair, wool, nails, horns, and feathers on living species. In the natural form, keratin is arranged into fibrillar structures or by intermolecular hydrogen bonding of peptide chains (Kelsall et al., 2005).

Globular proteins are useful biological substances that make up enzymes, transport proteins, and may contain  $\alpha$ -helix and/or  $\beta$ -helix secondary structures (Kelsall et al., 2005).

Relative to synthetic self-assembling materials, DNA fragments in a solution form lyotropic liquid crystals. In reference to Fig. 10.1, the short fragments behave like rods as illustrated, thereby forming liquid crystal phases. By increasing the concentration of the solution, self-organization of cholesteric (twisted nematic phase) and columnar liquid crystal phases may be observed (Kelsall et al., 2005). The structures of the preceding phases are shown in Fig. 10.2A and B.



**FIGURE 10.2**

(A) Nematic twisting of cholesteric phase and (B) hexagonal columnar phase.

From (A) Barrett Research Group. (n.d.). *Introduction to liquid crystals*. Retrieved 31.03.11, from McGill University: [http://barrett-group.mcgill.ca/teaching/liquid\\_crystal/LC03.htm](http://barrett-group.mcgill.ca/teaching/liquid_crystal/LC03.htm); (B) *Organic and Biomolecular Chemistry*. (2009). Retrieved 31.03.11, from Royal Society of Chemistry: <http://www.rsc.org/publishing/journals/ob/article.asp?Type=Issue&Journalcode=OB&Issue=16&SubYear=2009&Volume=7&Page=0&GA=on>.

The biological self-organization of microtubules plays an important role in nanotechnology development. Microtubules are formed from protein tubulin. At the nanoscale, these structures can be used as nanochannels to transport liquids or as struts to support nanostructures. The importance of this substance in eukaryotes is of interest in the field of nanotechnology. Fig. 10.3 shows the structure of a microtubule (Kelsall et al., 2005).

Cilia, which are hair-like strands, move to allow fluid across the surface of organs, therefore the sliding of subfibers formed from microtubules shown in Fig. 10.3 influences the efficient motion of the cilia. In nanotechnology, it is currently under study to see if nanomotors like those used in cilia will be incorporated into nanomachines or will inspire designs for artificial motors (Kelsall et al., 2005).

The final biological self-assembling material that will be discussed is viruses. The structure of a virus takes the form of a sphere or helical (rod-like shape). Viruses are comprised of nucleic acid molecules encased in a protein coat and therefore often termed as virus capsids. Fig. 10.4 shows some of the common viruses (Kelsall et al., 2005).

Fig. 10.4A shows the self-assembled icosahedral structure of the herpes virus. The rhinovirus also takes on this structure. Fig. 10.4B and C illustrates the self-organized helical structure of the tobacco virus which was the first virus to be discovered. The dimensions of the tobacco mosaic virus in this figure are approximately 300 nm in length and 18 nm in diameter (Kelsall et al., 2005).

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### 10.3 PRINCIPLES OF SELF-ASSEMBLY

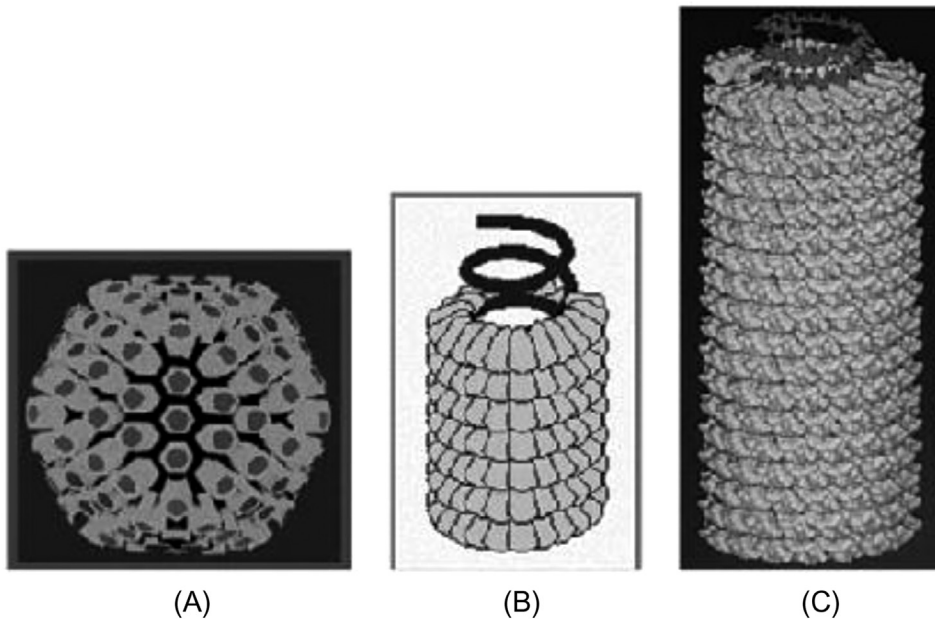
Self-assembly is the reversible and cooperative assembly of predefined parts into an ordered structure, which assembles with no external influences after the initial trigger. Currently, self-assembly has been broken down into two categories: static and dynamic. Static self-assembly refers to systems at equilibrium which do not dissipate energy. The formation of the nanostructure may require energy, but the structure is stable once it has been formed. Dynamic self-assembly refers to the formation or patterning of structures when the system does, in fact, dissipate energy.



**FIGURE 10.3**

X-ray structure of a microtubule.

*From Kelsall, R., Hamley, I., & Geoghegan, M. (2005). Nanoscale science and technology. Hoboken: John Wiley & Sons Ltd.*

**FIGURE 10.4**

(A) Structure of herpes simplex virus protein shell; (B and C) tobacco mosaic virus.

*From Kelsall, R., Hamley, I., & Geoghegan, M. (2005). Nanoscale science and technology. Hoboken: John Wiley & Sons Ltd.*

Self-assembly in materials relies on the fact that the fluctuations in the orientation and position of the molecules or particles due to random movements have energies in the order of thermal energy. The use of thermal energy in changing material properties is quite prevalent in all industries, but the effect is even more important on the nanoscale. Thermal energy has a significant impact on materials on the nanoscale as non-covalent bonds are often broken and reformed in a new manner. Due to these non-covalent interactions between molecules, structure changes can be obtained by changes in the conditions provided for the molecules. For instance, temperature and pH changes help to initiate the transition of a structure to another.

### 10.3.1 NON-COVALENT INTERACTIONS

In order for self-assembly to occur, the non-covalent forces between the molecules need to be broken and reformed. As such, the forces between the molecules must be much weaker than the covalent bonds which hold the molecules together (Kelsall et al., 2005). In doing so, the molecules are not changed chemically, but are structured in a different orientation. The weak intermolecular interactions that govern molecular ordering in materials include hydrogen bonds, ionic interactions, dipolar interactions, van der Waals forces, and hydrophobic interactions.

Hydrogen bonding is especially important in biological systems. Protein structures in water are held together by hydrogen bonds (Kelsall et al., 2005). Hydrogen bonds are weaker than covalent bonds



(about 20 kJ/mol compared to about 500 kJ/mol for hydrogen bonds and covalent bonds, respectively) (Kelsall et al., 2005). As a result, structures can self-assemble without chemical reactions needing to occur, and the bonds are strong enough to hold the structures together once they have been formed.

Dipolar interactions follow the same principles as hydrogen bonding, except they are not limited to just hydrogen atoms. Dipolar interactions refer to the direct interactions between two magnetic dipoles. The dipoles are a result of the difference in electronegativity within molecules creating partial positive and negative charges within the molecule.

The van der Waals forces are the sum of the attractive or repulsive forces between molecules—other than those due to covalent bonds. The forces include those between a permanent dipole and a corresponding dipole, as well as the London dispersion forces.

The hydrophobic effect arises when a nonpolar solute is inserted into water. The hydrophobic effect is attributed to the ordering of water molecules around a hydrophobic molecule. The ordering leads to a reduction in entropy (Kelsall et al., 2005). The entropy loss can be offset when association of hydrophobic molecules into micelles occurs, as this results in an increase in entropy.

### 10.3.2 INTERMOLECULAR PACKING

At higher concentrations, the packing of block copolymer or amphiphilic molecules in solution leads to the formation of lyotropic liquid crystal phases (Kelsall et al., 2005). These crystal phases include cubic-packed spherical micelles, hexagonal-packed cylindrical micelles, lamellae, and bicontinuous cubic phases. The lyotropic crystal phases are illustrated in Fig. 10.5.

The phase that forms is dependent on the curvature of the surfactant–water interface. To understand the lyotropic phase behavior, there exist two approaches. The first approach computes the free energy associated with curved interfaces; the curvature is analyzed using differential geometry, while not incorporating details of the organization of the molecules (Kelsall et al., 2005). The second approach uses a molecular packing parameter to describe the interfacial curvature (Kelsall et al., 2005).

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## 10.4 METHODS TO PREPARE AND PATTERN NANOPARTICLES

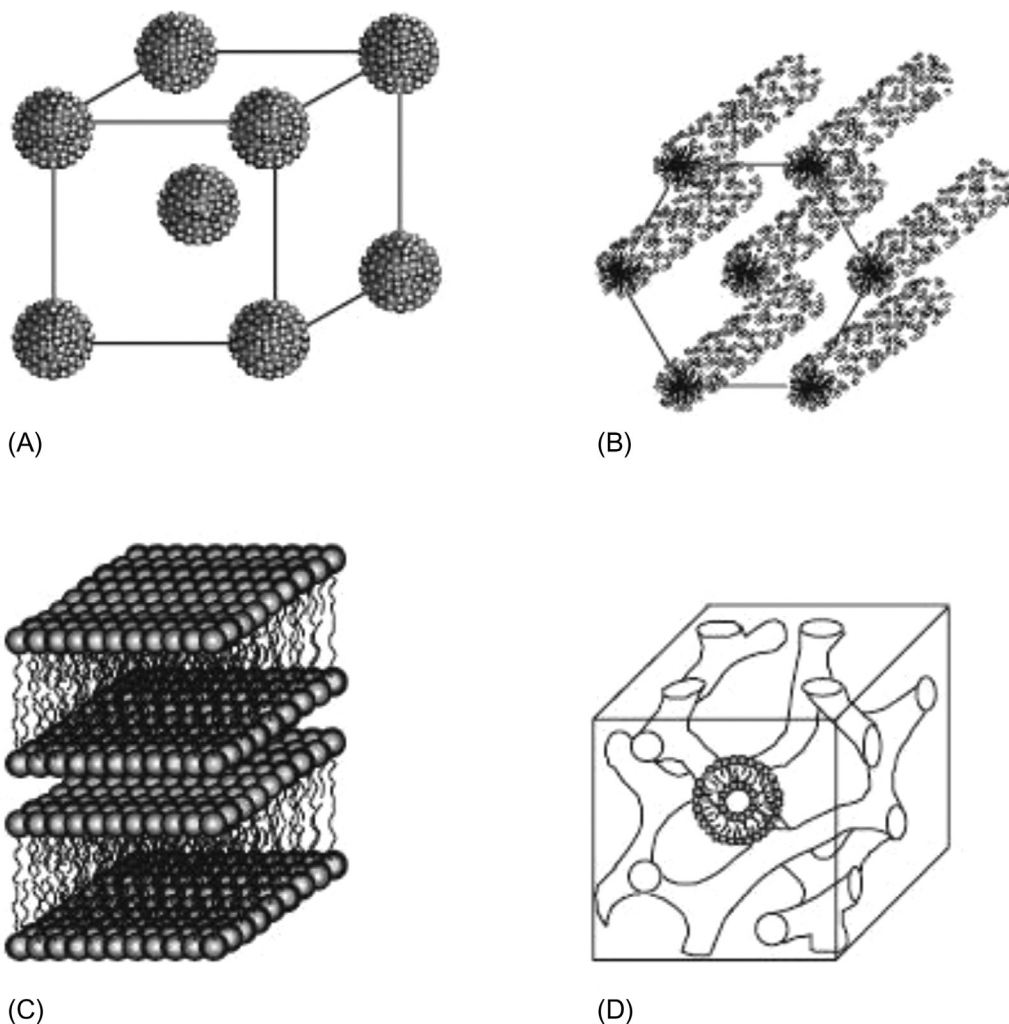
### 10.4.1 NANOPARTICLES FROM MICELLAR AND VESICULAR POLYMERIZATION

One of the main challenges in nanotechnology is the fabrication of nanoparticles of certain, and controlled, size, shape, as well as functionality (Kelsall et al., 2005). There are several established routes to nanoparticle preparation. Spherical nanoparticles can be prepared by fine milling. Metal and metal oxide nanoparticles can be prepared using micellar nanoreactors.

Additionally, metal nanoparticles can be surface-patterned using the self-organization of block copolymers. For metal nanoparticles, a method of patterning is the nanoparticle formation occurring within micelles in solution, which is then deposited on a solid substrate. Another method of patterning metal nanoparticles is the direct patterning by way of selective wetting.

Nanocapsules can be prepared by employing cross-linking of the shell of the block copolymer vesicles (Kelsall et al., 2005). Another method is to use polyelectrolyte multilayers that are assembled around a colloidal core, which dissolves.



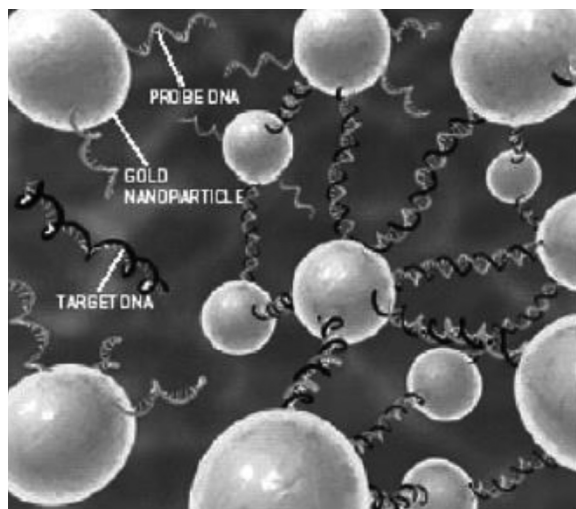
**FIGURE 10.5**

Lyotropic liquid crystal structures: (A) cubic-packed spherical micelles, (B) hexagonal-packed cylindrical micelles, (C) lamellar phase, and (D) bicontinuous cubic structure.

*From Kelsall, R., Hamley, I., & Geoghegan, M. (2005). Nanoscale science and technology. Hoboken: John Wiley & Sons Ltd.*

### 10.4.2 FUNCTIONALIZED NANOPARTICLES

With the ability to specify functionality for nanoparticles, there can be a whole new set of applications. Functionalized nanoparticles are already used in the medical field. Gold nanoparticles functionalized with proteins have been used as indicators to detect biological molecules, as well as changes in

**FIGURE 10.6**

DNA-functionalized gold nanoparticle gene sequence detection system.

*From Kelsall, R., Hamley, I., & Geoghegan, M. (2005). Nanoscale science and technology. Hoboken: John Wiley & Sons Ltd.*

biological systems (Kelsall et al., 2005). Using dip pen nanolithography, arrays of nanoparticles can be prepared. A specific example is presented in Fig. 10.6, where functionalized nanoparticles are used for detecting specific gene sequences in genetic screening.

For detecting specific gene sequence, the sequence of bases in target DNA is identified. Two sets of gold nanoparticles are then prepared. One set has attached DNA that binds to one end of target DNA, while the other carries DNA that binds to the other end. Upon addition of target DNA, the two types of nanoparticles are bound together, forming an aggregate. The formation of the aggregate results in a shift in the light-scattering spectrum from the solution. A color change in the solution occurs and can be detected easily (Kelsall et al., 2005).

### 10.4.3 COLLOIDAL NANOPARTICLE CRYSTALS

Photonic band gap crystals have been receiving a lot of attention due to their ability to confine photons or control stimulated light emission, as well as constructing lossless waveguides (Kelsall et al., 2005). A photonic band gap crystal is a structure that has periodic variation in its dielectric properties. By forming face-centered cubic lattices from colloidal spheres, it has been learned that independent of the dielectric contrast, there is never a complete band gap. There is considerable effort being put forth into creating a complete three-dimensional (3D) band gap. In order to do so, the colloidal particles must have low dispersity (so as to form a cubic crystal), and the number of defects must be minimized (Kelsall et al., 2005).

Using so-called convective self-assembly, ordered crystals can be created by rapid evaporation of solvent, leaving the crystals alone on the surface. Another technique is the controlled withdrawal of

the substrate from a colloidal solution, where lateral capillary forces induce crystallization of spheres; if the meniscus is swept slowly across the substrate, well-ordered crystals may be deposited (Kelsall et al., 2005). Finally, an epitaxial mechanism may be employed, using lithographically patterned polymer substrate to template crystal growth (Kelsall et al., 2005). For this mechanism, holes are created in a rectangular array, with sizes large enough to just hold one colloidal particle. Layer-by-layer growth can be achieved by slow sedimentation of the silica spheres that were used initially. Hollow or solid nanoparticles can be grown, allowing for the possibility of preparing colloidal crystals of solid or hollow  $\text{TiO}_2$  particles, as well as conductive polymer nanoparticles (Kelsall et al., 2005).

#### 10.4.4 SELF-ORGANIZING INORGANIC NANOPARTICLES

There is a growing interest in composite materials that have a polymer with filler particles such as clay particles. The fillers effectively modify the properties of polymer, improving transport, mechanical and thermal properties by 10-folds, and higher orders of magnitude. The polymer-clay nanoparticles tend to be lighter, while offering identical mechanical performance (Kelsall et al., 2005). Moreover, the mechanical properties for the polymer-clay nanoparticles are superior to fiber-reinforced and other polymers, because there is reinforcement in two dimensions from the inorganic layers, as opposed to one (Kelsall et al., 2005). Finally, the polymer-clay nanoparticles offer exceptional diffusional barrier properties, without requiring additional layers as part of the design. The particles are formed using silicate layers which are combined with layers of octahedrally coordinated atoms of aluminum or magnesium (Kelsall et al., 2005). The layers result in the clay being in a lamellar phase when in water.

#### 10.4.5 LIQUID CRYSTAL NANODROPLETS

Liquid crystal droplets being patterned at the nanoscale has the potential for applications in phased array optics. In phased array optics, 3D images are reconstructed on a two-dimensional surface (Kelsall et al., 2005). Phased array optics allows this to happen if the amplitude and the phase of the light waves emitting from the virtual image are controlled. To reconstruct a light wave pattern, an array of switchable light sources 200 nm apart is sufficient in most cases (Kelsall et al., 2005). However, liquid crystals can be used as switchable phase shifters, hence their use in phased array optics. Patterning of liquid crystals in micelles is a proposed and promising method of arranging liquid crystals for nanoscale arrays (Kelsall et al., 2005).

#### 10.4.6 BIONANOPARTICLES

Bionanoparticles are structures on the nanoscale that are biological, as opposed to synthetic. Viruses are natural nanoparticles, and a number of nanotech applications of viruses are now being considered. Viruses are used as responsive delivery agents. Modified cowpea chlorotic mottle virus nanoparticles have been used as biocompatible responsive delivery agents (Kelsall et al., 2005). The virus is a compact spherical structure, but as pH is increased above 6.5, the structure becomes porous, allowing the pH-controlled release of the drug. For nonviral gene delivery, synthetic polymers including polylysine and poly(oxyethylene)-based copolymers, biologically derived liposomes, cationic lipids, and cationic polyelectrolyte poly(ethyleneimine)—called PEI—have been studied. PEI is useful for binding anionic

DNA within the physiological pH range and forcing DNA to form condensates, which can be effectively transferred across the cell membrane (Kelsall et al., 2005).

### 10.4.7 NANOOBJECTS

Particles have been prepared with shapes other than the traditional spheres, shells, or tubes, at the nanoscale. Nanoprisms have been prepared using conversion via photoinduction. Nanocrystal growth can be controlled using organic agents, resulting in the production of polyhedra, with the growth rate of planes in crystal unit cell controlling the faces (Kelsall et al., 2005). String and other structures can be prepared using surfactants to selectively control the growth of certain crystal faces. Self-assembled nanostructures can also be employed to template the formation of helical nanoparticles, as well as vesicular or string structures formed by block copolymers (Kelsall et al., 2005).

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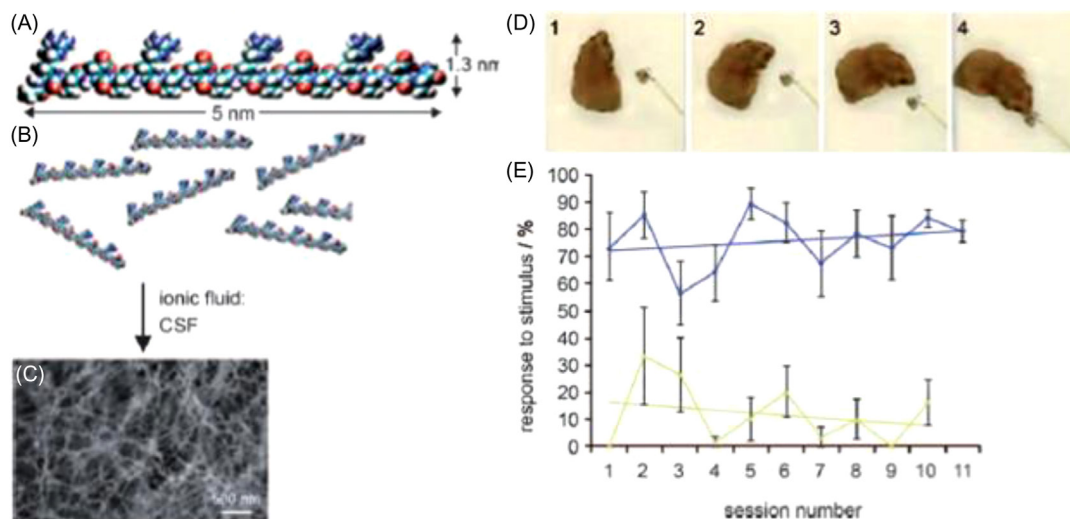
## 10.5 CURRENT RESEARCH AND FUTURE PERSPECTIVES

Because self-assembly has much potential for a variety of applications, much research is dedicated to using and improving this method. This section discusses current research for applications in Li-ion batteries, supercapacitors, hydrogels, water treatment, and optical cable, displays, filters and sensors.

Hirst, Escuder, Miravet, and Smith (2008) reviewed the ability of self-assembled peptide nanofiber (hydrogel) to regenerate the optic tract and functional recovery of vision. Zhang and coworkers applied a nanoscaffold supported by a gelator with a peptide repeat unit of Arg-Ala-Asp-Ala to successfully enable reconnection of nerve tissue after optical tract in a hamster's midbrain had been surgically severed (Ellois-Behnke et al., 2006). The 1% concentrated peptide nanofiber solution was injected into the test hamster and regenerative results were compared to those of an untreated hamster. The optic tract in the treated hamster was able to regenerate and functional vision was restored, whereas no axonal regeneration in the untreated hamster was observed. From the same procedure, it was also discovered that the self-assembling peptide gel could be applied to a wound and achieve complete hemostasis in 15 s (Fig. 10.7).

Based on the results of Zhang, the authors propose that healing can be accelerated by close contact between the self-assembled nanofibers and the extracellular matrix to assist cell-scaffold interactions. Six months after hydrogel treatment, there was no support to indicate the existence of prion-like substances or fibril entanglements in the treated animals. The study concluded that there is potential to assemble hydrogels to generate or exhibit distinct forms of biological activity, at a time when there is a greater understanding of nanoscale self-assembly processes.

The field of electro-optic nanotechnology has many applications in sensors and other nanostructure devices. Tsang et al. (2008) discussed the self-assembly of nanocrystals into large colloidal crystals, in which the secondary structures are manipulated to fabricate nanoparticles as 3D regular structures, used for optical filters and other nanostructured devices. They developed a method to synthesize centimeter long magnetic colloidal crystals using magnetic gradient separation of chemical or biological entities. The large colloidal crystals are composed of 3D regular arrays of supermagnetic FePt nanoparticles encapsulated in a hydrophilic silica shell. The prepared sample underwent controlled crystallization followed by exposure to an external magnetic field. Fig. 10.8 shows the needle-shaped crystals approximately 1 cm in length and the stacking of nanoparticles.



**FIGURE 10.7**

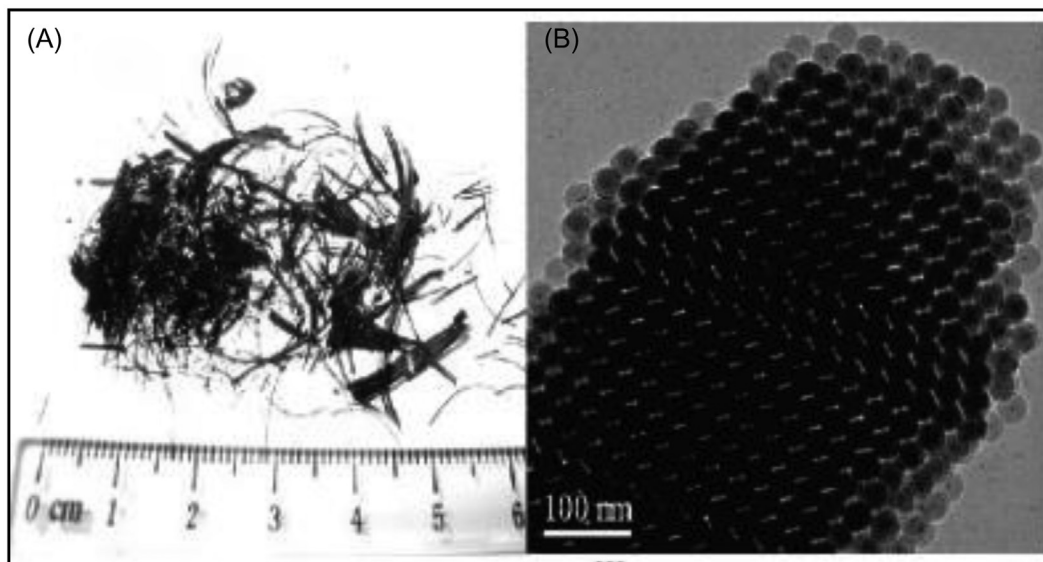
Peptide hydrogelators assemble into a fibrillar network as a consequence of hydrophobic and hydrogen bond interactions (A–C). When applied to the damaged optic nerve of hamsters blinded in their right eye, vision is regenerated and the hamster responds to stimulus (D). The data in (E) indicate that treated hamsters (blue (black in print version)) regained 80% vision, whereas untreated animals (yellow (gray in print version)) regained less than 20%.

From Hirst, A., Escuder, B., Miravet, J., & Smith, D. (2008). High-tech applications of self-assembling supramolecular nanostructured gel-phase materials: from regenerative medicine to electronic devices. *Angewandte Chemie International Edition*, 47, 8002–8018.

In this article, Tsang et al. (2008) shows the ability to manipulate secondary structured nanoparticles from self-assembly colloidal crystals into high-quality colloid crystals via magnetic crystallization of FePt-encapsulated silica shell. This approach opens up new development of high-quality nanostructured material that may potentially be used for optical filters, waveguides, sensors, and other nanodevices.

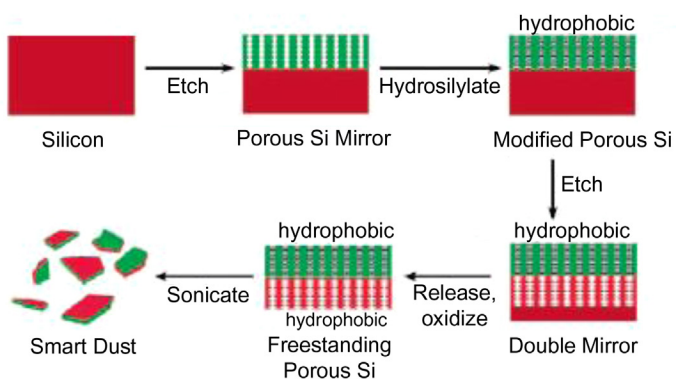
Link and Sailor (2003) discuss the development of Smart Dust—photonic crystals of porous Si—which is useful for various optics and sensor applications. They examine the method of electrochemical etching and surface chemistry, followed by the mechanism of self-assembly and self-orientation of colloidal photonic crystals to produce Smart Dust. The material is prepared using a two-step method. In the first step, an electric current is used in the electrochemical etching of Si, to produce a one-dimensional photonic crystal. In the second step, the porous Si photonic structure is chemically modified. As a result a thin film is produced and fractured into nanostructured smaller particles with the ability to self-assemble. Fig. 10.9 is a detailed flow diagram of the synthesis of Smart Dust particles.

The preceding technique manipulates matter at the nanoscale to develop nanostructured material and devices by self-assembly. In this study, when introduced at a liquid interface, the fractured Smart Dust particles self-orient spontaneously with the hydrophobic side facing up. Smart Dust particles can be

**FIGURE 10.8**

(A) Needle-shaped crystals—3 nm FePt colloidal crystals inside 33 nm silica sphere and (B) transmission electron microscopy (TEM) image of hcp arrangement of encapsulated nanoparticles.

From Tsang, S., Yu, C., Tang, H., He, H., Castelleto, V., Hamley, I., et al. (2008). Assembly of centimeter long silica coated FePt colloid crystals with tailored interstices by magnetic crystallization. *Chemistry of Materials*, 4554–4556.

**FIGURE 10.9**

Synthesis of bifunctional Smart Dust particles.

From Link, J. R., & Sailor, M. J. (2003). Smart Dust: self-assembling, self-orienting photonic crystals of porous Si. *Proceedings of the National Academy of Sciences*, 10607–10610.

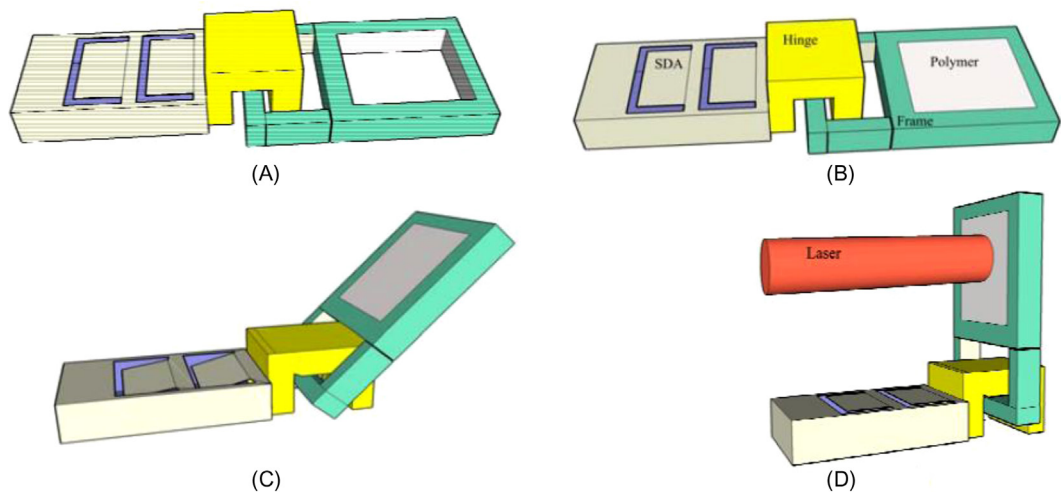


used in information display, optical switching, chemical and biological sensor fields, high-throughput screening, and drug discovery.

Zhang, Le, Malalur-Nagaraja-Rao, Hsu, and Chiao (2005) propose a solution to challenges of manufacturing in the optical communication and sensor industry. Micro-optical components require expensive alignment and assembly procedures. The development of a self-assembled, micro-optical component may thus be a solution. Self-assembly of 3D microstructures was designed to eliminate manual or robotic manipulations that are costly and sometimes inaccurate. The design was conducted using MEMS fabrication foundry service—MUMPS (Multi-user MEMS Process). Fig. 10.10 shows the mechanical design of the device. A scratch disk actuator is hinged to a polysilicon frame. The direction of motion of the actuator is a straight path controlled by applied voltages. The hinges allow for out-of-plane, perpendicular assembly.

The application of a polymer on the polysilicon frame results in good optical transparency and shows good mechanical properties for the assembly process. Optical performance of the filter had been yet to be examined.

Certain optical and electronic devices are fullerene-based. Georgakilas, Pellarini, Prato, Guldi, and Melle-Franco (2002) examined an assembly method to produce the formation of nanotubular structures. The authors decided on using fullerenes for their self-assembly process because they have excellent electronic properties and because their derivatives were found to self-assemble at the nanoscale. Four different compounds were prepared and immersed in ultrasonic baths before being transferred to TEM. Fig. 10.11A and B shows TEM images for the first and second compounds. It was observed



**FIGURE 10.10**

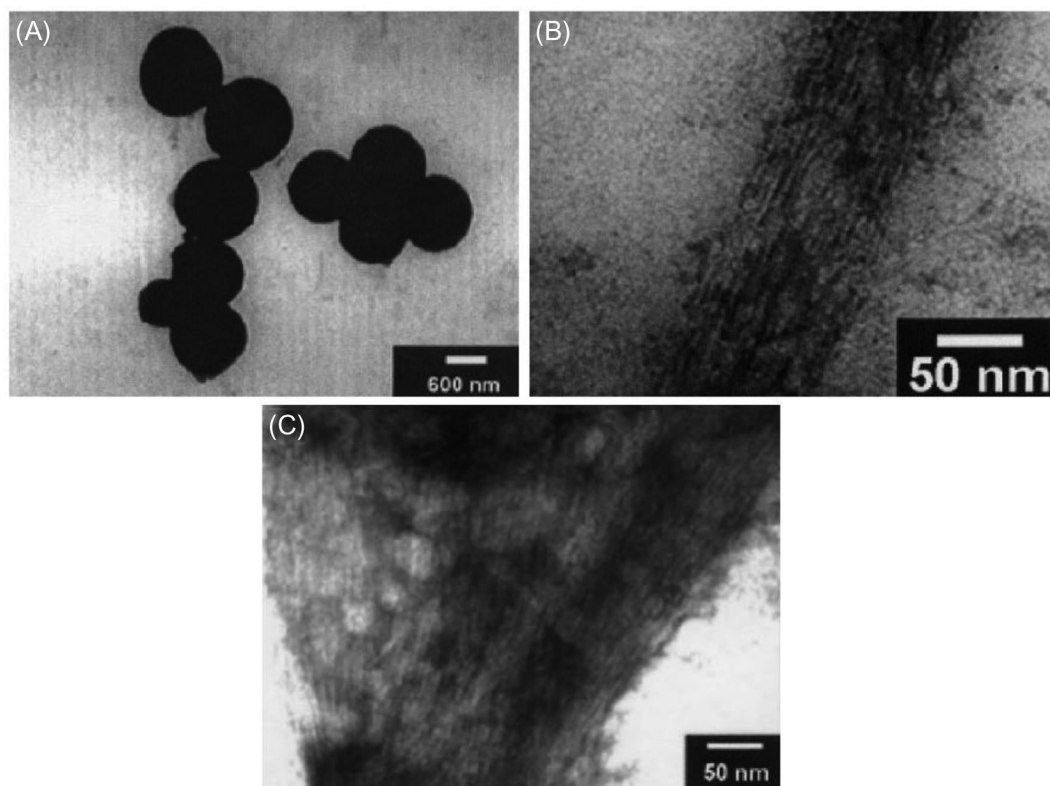
Device architecture. (A) Scratch drive actuators (SDA) is connected to hinged polysilicon frame; (B) polymer film acts as optical interface on polysilicon frame; (C) actuators lift up frame; (D) the frame stands perpendicular to the substrate after assembly with a laser shone normal to the filter surface.

*From Zhang, P., Le, K., Malalur-Nagaraja-Rao, S., Hsu, L., & Chiao, J. (2005). Self-assembly micro optical filters. Society of Photographic Instrumentation Engineers.*



that spheres were formed by compound 1, while bundles of nanorods were formed by compound 2. Fig. 10.11C shows nanorods formed by compound 3, while compound 4 produced neither rods nor spheres, but isolated tubules. They also observed that ligation of compound 2 with a porphyrin moiety promoted the formation of nanorods with strongly improved shaping.

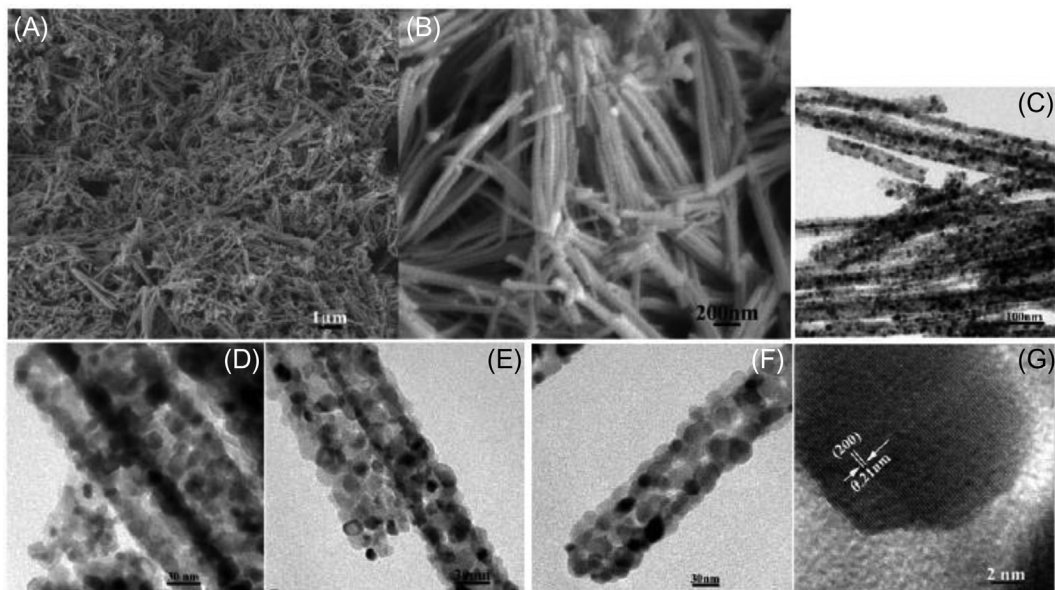
Much nanotechnology research is continuously performed in the electrical and electrochemical fields. One important application is making and improving energy storage devices. Xiong, Yuan, Zhang, and Qian (2011) examined the potential advantage of NiO nanostructures as supercapacitor materials. They used NiO quasi-tubular structures by self-assembly of nanoparticles as basis for illustration (Fig. 10.12). They prepared various NiO hierarchical nanostructures by heating the corresponding self-assembled NiO hierarchical nanostructure precursors at 300°C for 2 h at a heating rate of 1°C/min. The self-assembled NiO quasi-tubular nanostructure in an amount of 75 wt% was mixed with



**FIGURE 10.11**

(A) TEM images for compound 1. The images showed spheres being formed. (B) TEM image of a bundle of nanorods formed by compound 2. (C) TEM image of a bundle of nanorods formed by compound 3.

*From Georgakilas, V., Pellarini, F., Prato, M., Guldi, D. M., & Melle-Franco, M. (2002). Supramolecular self-assembled fullerene nanostructures. Proceedings of the National Academy of Sciences, 5075–5080.*



**FIGURE 10.12**

(A and B) Field-emission scanning electron microscopy (SEM) images and (C–F) TEM images of the as-obtained NiO quasi-tubular structures by self-assembly of nanoparticles. (G) High-resolution TEM image taken from an individual nanoparticles self-assembling into NiO quasi-tubular structures.

From Ziong, S., Yuan, C., Zhang, X., & Qian, Y. (2011). Mesoporous NiO with various hierarchical nanostructures by quasi-nanotubes/nanowires/nanorods self-assembly: controllable preparation and application in supercapacitors. *CrsytEngComm*, 13, 626–632.

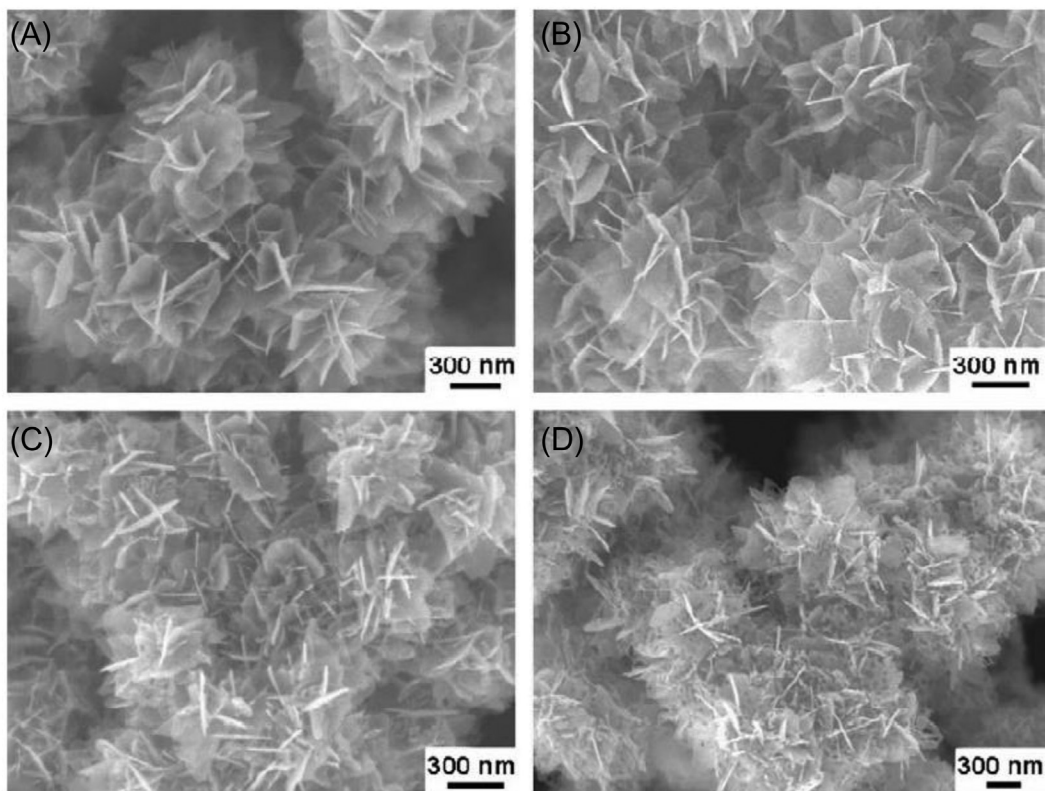
20 wt% of acetylene black and 5 wt% of poly(tetrafluoroethylene) and pressed (20 MPa) onto a nickel grid (1 cm<sup>2</sup>) for assembly of the test electrode. These rich in porosity nanostructures have large specific surface areas that promote efficient contact with more electroactive sites for electrolyte, even at high current densities.

They observed the self-assembled quasi-tubular structures to display high specific capacitance (SC) and its ability to retain SC at higher current densities. The NiO quasi-nanotubes are able to maintain a SC of 345 F/g after 1500 continuous charge–discharge cycles, relative to the initial SC of 314 F/g. Therefore, the NiO quasi-tubular structures self-assembled with nanoparticles have demonstrated their excellent capacity retention of 91% after 1500 continuous charge–discharge cycles and high rate capability. Excellent electrochemical performance data of these easy to assemble NiO quasi-tubular structures suggest they have potential use in applications such as supercapacitors and Li-ion batteries.

Yang et al. (2010) examined the ability of a self-assembled 3D flower-shaped SnO<sub>2</sub> nanostructure to be used as an anode in Li-ion batteries. The flower-shaped SnO<sub>2</sub> nanostructure was self-assembled by hydrothermal treatment of a mixture of tin (II) dichloride dehydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) and sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O) in a continuously stirred solution of distilled water and sodium hydroxide (NaOH) (Yang et al., 2010). The electrochemical performance of the SnO<sub>2</sub> nanostructure in the potential range of 0.005–1.5 V was tested for up to 30 cycles and the results were compared against commercially

used carbon-based materials. The authors observed that nonconductive impurities (such as hydroxides and organic material) that remain on the nanostructure following the hydrothermal synthesis reduce the overall conductivity and the irreversibility during charge and discharge cycles. To solve the issue, the SnO<sub>2</sub> nanostructures were heat-treated in air above 400°C to remove the hydroxides and decompose the organic impurities. The electrochemical performance of the heat-treated nanostructures was improved over the unheated sample. Fig. 10.13 depicts SEM images of the SnO<sub>2</sub> heat-treated at various temperatures, and Fig. 10.14 compares the electrochemical properties of the heat-treated samples from Fig. 10.13.

When the flower-like SnO<sub>2</sub> nanostructures are used as anode material for Li-ion batteries, they demonstrate a reversible capacity of approximately 670 mA·h·g<sup>-1</sup> after 30 cycles, which is almost double



**FIGURE 10.13**

SEM images of the SnO<sub>2</sub> nanostructures prepared after calcinations in air at different temperatures: (A) as-synthesized nanostructures obtained by hydrothermal treatments; (B) after heating in air at 300°C, (C) 400°C, and (D) 700°C, respectively.

*From Yang, R., Gu, Y., Li, Y., Zheng, J., & Li, X. (2010). Self-assembled 3D flower-shaped SnO<sub>2</sub> nanostructures with improved electrochemical performance for lithium storage. Acta Materialia, 58, 866–874.*

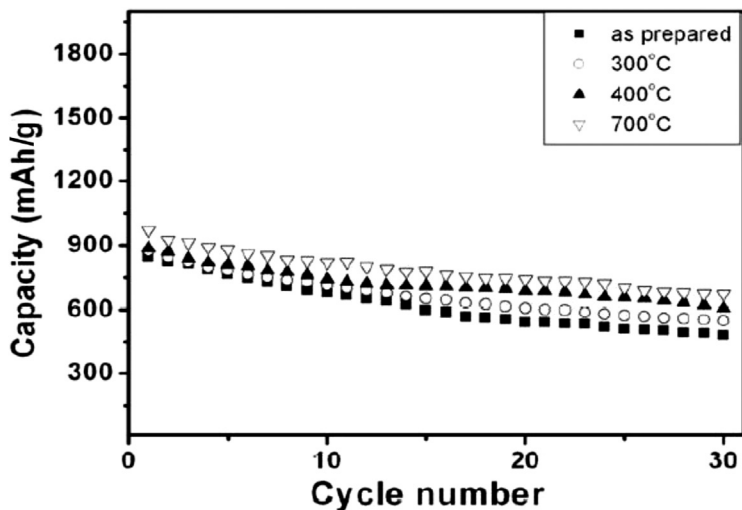


FIGURE 10.14

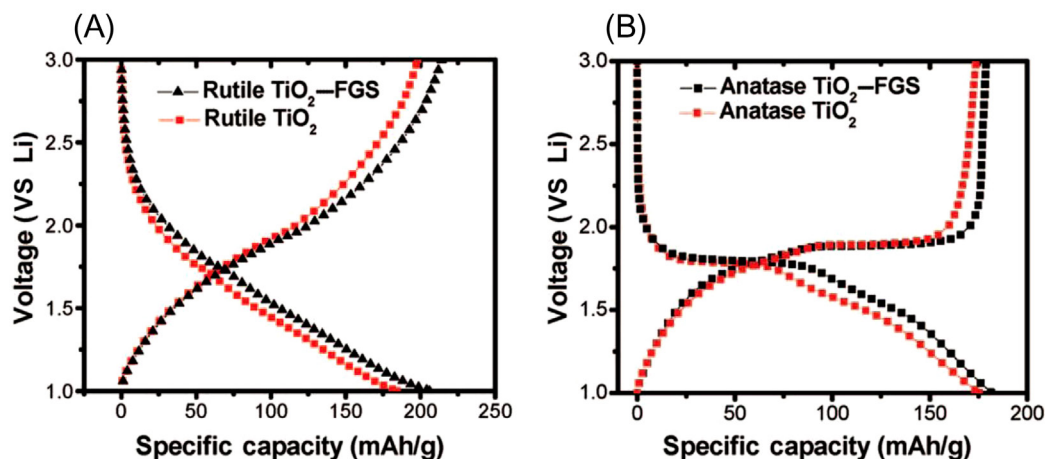
Charge capacities of the heat-treated (in air) SnO<sub>2</sub> nanostructures.

From Yang, R., Gu, Y., Li, Y., Zheng, J., & Li, X. (2010). Self-assembled 3D flower-shaped SnO<sub>2</sub> nanostructures with improved electrochemical performance for lithium storage. *Acta Materialia*, 58, 866–874.

the reversible capacity of the commercially used carbon-based materials (372 mA·h·g<sup>-1</sup>) (Dahn, Zheng, Liu, & Zue, 1995). In addition, the average capacity loss of the flower-like 3D nanostructure was estimated to be 0.95% per cycle after the second cycle, smaller than that of pristine SnO<sub>2</sub> particles (3.46%). The study concluded that the improved electrochemical performance of the self-assembled 3D SnO<sub>2</sub> nanostructures indicates that these nanostructures can enhance the electrochemical properties of anode materials for Li-ion batteries.

There are many other studies that may prove useful for Li-ion battery improvement. Wang et al. (2009) examined the insertion and extraction kinetics for Li ions using functionalized graphene sheets (FGSs). They created hybrid nanostructures to observe the effects on the kinetics for Li ions during insertion and extraction. TiO<sub>2</sub> was chosen as the metal oxide and prepared as the hybrid with FGS. Both rutile and anatase TiO<sub>2</sub> were used to study the effects. Using sonification, sodium dodecyl sulfate (SDS)–FGS dispersions were prepared. The SDS surfactant helps promote the formation of the TiO<sub>2</sub> hybrid nanostructures, as it determines the interfacial interactions between graphene and the oxide materials. As crystalline TiO<sub>2</sub> formed, nanoparticles began coating the graphene surface due to the sulfate head groups having strong bonding with TiO<sub>2</sub>. The hybrid nanostructure, TiO<sub>2</sub>–graphene, enhanced Li-ion insertion and extraction kinetics, particularly for higher charge and discharge rates. Fig. 10.15A and B shows the improved specific capacity for the hybrid nanostructures over the metal oxides alone.

From this, it was concluded FGS should serve as a conductive additive for Li-ion battery electrode materials to improve diffusion, electron transport, and lower the resistance at the interface of electrodes and electrolytes.



**FIGURE 10.15**

(A) Charge–discharge profiles for control rutile TiO<sub>2</sub> and rutile TiO<sub>2</sub>–FGS hybrid. (B) Charge–discharge profiles for anatase TiO<sub>2</sub> and anatase TiO<sub>2</sub>–FGS hybrid.

From Wang, D., Choi, D., Li, J., Yang, Z., Nie, Z., Kou, R., et al. (2009). Self-assembled TiO<sub>2</sub>–graphene hybrid nanostructures for enhanced Li-ion insertion. *American Chemical Society*, 907–914.

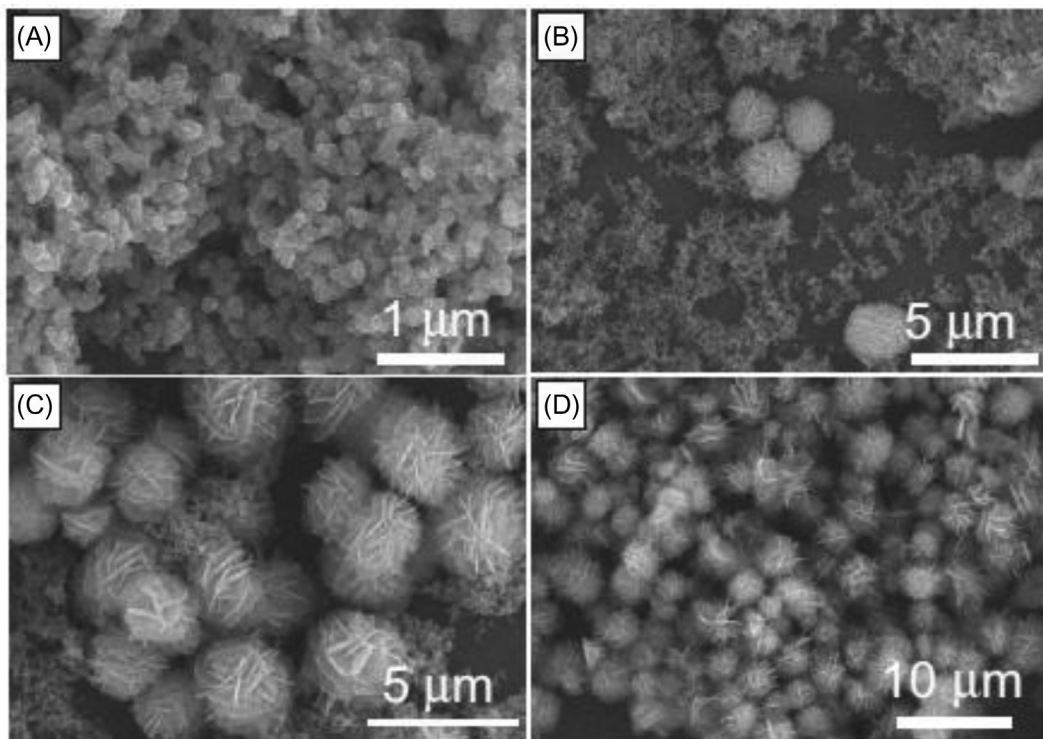
Self-assembly has also been studied outside the electronic and electro-optical fields. For example, Zhong, Hu, Liang, Cao, and Song (2006) investigated synthesizing an iron oxide precursor with 3D flower-like nanostructure using an ethylene glycol-mediated process, and then using it for treating wastewater. Ferric chloride was used as the source for iron. Ferric chloride, urea, and tertbutylammonium bromide were dissolved in ethylene glycol. Once the iron oxide precursor had been formed, it was collected and the morphology of the precursor was studied by SEM. Fig. 10.16 shows the formation of the 3D flowerlike nanostructures as the reaction proceeds. Fig. 10.16A shows the nanoparticles being formed, then beginning to cluster in (B). In Fig. 10.16C, the clusters start taking the flowerlike shape, and by (D) the sample became composed of entirely 3D flowerlike nanostructures.

Once the nanostructures were created, they were employed in wastewater treatment. Arsenic and chromium were the two major components that needed to be removed, and the iron oxide was able to do so with an adsorption capacity of 5.3 mg As/g and 4.47 mg Cr/g. It was concluded that the as-prepared iron nanostructures should be able to remove heavy metal ions and other pollutants in water treatment extremely well.

## 10.6 CONCLUSIONS

In this chapter, the definition and importance of self-assembled nanostructures were highlighted. The principles of self-assembly were discussed and applications of self-assembled nanostructures were reviewed. Self-assembly is considered to be one of the simplest methods to synthesize nanostructures.





**FIGURE 10.16**

SEM image as the reaction proceeded at time (A) 2 min, (B) 6 min, (C) 7 min, and (D) 8 min.

*From Zhong, L., Hu, J., Liang, H., Cao, A., & Song, W. (2006). Self-assembled 3D flowerlike iron oxide nanostructures and their application in water treatment. Advanced Materials, 2426–2431.*

However, there still remains a great challenge to fabricate hierarchically self-assembled nanostructures with specified chemical components and controlled morphologies (Yang et al., 2010). Nanostructures can be self-assembled from molecular materials and devices to exhibit advanced properties that can be achieved through the application of external fields, typically by simple hydrothermal or magnetic treatment.

The primary focus of [Section 10.5](#) is the fabrication of 3D nanostructures prepared by simple hydrothermal or magnetic self-assembly processes. The formulated 3D nanosuperstructures were applied as components in Li-ion batteries, supercapacitors, hydrogels, water treatment coagulants, and optical filters and sensors. Researchers have either proven advanced physical and chemical properties of the self-assembled nanostructures in specified applications or they have yet to explore that in research and development. Potential applications of the assembled nanostructures are suggested to provide insight into the broad spectrum to which their respective features can be applied.

Significant progress has been reported in the development and use of self-assembled nanostructures for application of their advanced properties, including the preparation of nanoparticles, patterning

of nanostructures, nanomotors, utilization of biomineralization, and for functionalized drug delivery (Kelsall et al., 2005). It is likely that the first nanostructures to be commercialized will be nanoparticles fabricated in micellar or vesicular nanoreactors, and catalysts and separation media fabricated from mesoporous templated materials (Kelsall et al., 2005). Self-assembly methods have proven to fabricate effective, efficient, and low-cost nanostructures. In the next few decades, there will be a creation of many new materials and nanosuperstructures as novel research in the field of nanotechnology is expected to increase exponentially. As the case with most scientific and technological breakthroughs, the rise and development of nanotechnology and self-assembled nanostructures can be expected to impact the quality of life of people everywhere—for better or for worse.