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Introduction

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On 29 December 1959, the great physicist Richard P. Feynman, one of the Laureates for the Nobel Prize in Physics 1965 "for their fundamental work in quantum electrodynamics, with deep-ploughing consequences for the physics of elementary particles", gave a far-reaching prophetic lecture entitled "There's Plenty of Room at the Bottom" at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech). He said "*What I have demonstrated is that there is room – that you can decrease the size of things in a practical way. I now want to show that there is plenty of room. I will not now discuss how we are going to do it, but only what is possible in principle – in other words, what is possible according to the laws of physics. I am not inventing anti-gravity, which is possible someday only if the laws are not what we think. I am telling you what could be done if the laws are what we think; we are not doing it simply because we haven't yet gotten around to it.*" [1]. Feynman said that "*The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom*". The past few decades have witnessed many inventions and discoveries in the preparation of nanoscale materials to authenticate his visionary prediction, and we can make nanoscale machine in the manner of arranging atoms one by one, and carry out chemical synthesis by mechanical manipulation.

Nanotechnology is the term used to cover the design, preparation, and applications of nanostructured systems. Nanotechnology also includes fundamental the understanding of physical properties and phenomena of nanostructures. The typical dimension for nanostructures spans from subnanometer to several hundred nanometers [2]. One nanomater (nm, one-billionth of meter, 10^{-9} m), is approximately the length equivalent to 10 hydrogen, or 5 silicon, or 3½ gold atoms aligned in a line. By convention, nanotechnology is taken as the structures at least one dimension in the range 1–100 nm following the definition used by the National Nanotechnology Initiative (NNI) in the US [3].

Nanotechnology has been becoming an important research fields, representing an assemblage of many sciences and technologies at the nanometer scale, which encompasses the synthesis and application of nanostructured systems with sizes ranging from individual atoms or molecules to submicron dimension, as well as the assembling the resulting nanostructures into larger systems [4]. The emergence of nanotechnology as a unique and powerful interdisciplinary

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research activity with significant societal impact has affected almost all areas of science and technology. It has resulted in distinguished materials with novel and/or significantly improved physical properties (such as, optical, electrical, magnetic properties, etc.); chemical, mechanical, biological properties compared to those of their bulk analogues. The properties of nanostructured materials are quite different from those at a large scale. Nanotechnology today is a creative fusing of bottom-up chemistry approach and top-down engineering approach. We are currently witnessing an eruption of novel strategies for making and manipulating, visualizing and interrogating nanostructured materials.

In 2000, United States federal government issued the NNI which is a program for the science, engineering, and technology research and development for nanoscale projects. Whereafter, the NNI initiated a nanotechnology windstorm around the world [3]. The cumulative NNI investment since fiscal year 2001, including the 2015 request, totals almost $21 billion. Most challenging in nanotechnology will be those areas that relate to nanofabrication, in particular the development of viable fabrication technologies which will lead to cost-effective nanomanufacturing processes [4].

In order to understand nanotechnology, we need to first understand some quantum mechanics. Quantum mechanism assumes importance as material size is diminished. This is especially true in nanoscience.

1.1 Wave-Particle Duality

Before the beginning of the twentieth century, there was a disagreement about the true nature of light, with the followers of Isaac Newton supporting a corpuscular theory, whereas the followers of Christiaan Huygens approved light of a wave motion. Thomas Young performed a double-slit experiment in 1801, when he showed that interference patterns could be produced when light was passed through two closely spaced slits [5]. The modern double-slit experiment demonstrates that light and matter can display characteristics of both classically defined a wave and a particle. The possession of both wave and particle properties is known as wave-particle duality, which is at the heart of quantum mechanics. The same is true of atoms, molecules, and subatomic particles such as electrons, photons, and neutrons. The wave-particle duality of matter means that an electron is essential neither a wave nor a particle but its motion can be quantified using the mathematical equations appropriate to waves and particles [6]. This phenomenon is thus far absolutely impossible to explain by using any classical manner. And the wave-particle duality is regarded as the best explanation we have thus far.

The double-slit experiment is one of the better ways to observe the quantum behavior of electrons in action. Based on the double-slit experiment, we can say about the electrons (the same being true of photons): they arrive one at a time, like particles, and their probability of arrival is subject to interference, like waves [7]. Detailed discussion of double-slit experiments can be found in the quantum mechanics book by Rae [8].

In 1924, Louis de Broglie postulated that matter exhibited a dual nature and proposed that the wavelength of a particular object of mass m is found from:

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{1.1}$$

where v is the velocity, mv is the momentum p of the object, $h = 6.63 \times 10^{-34}$ J s^{-1} is the Planck constant, and λ is called de Broglie wavelength here. The resulting waves are called matter waves. In the case of atomic structure, matter waves for electrons are standing waves that correspond to particular electron orbitals [6]. Electrons occupy regions of space, enclosing an atom's nucleus, which is called orbitals. These orbitals are organized into levels and sublevels, depending on how much energy the electrons have. The closer the nucleus the electrons occupy, the lower energy levels they have.

1.2 Uncertainty Principle

In relation to the double-slit experiment with electrons, the Uncertainty Principle, introduced first in 1927, by Werner Heisenberg, signifies that no device can be built to tell us which slit the electrons go through without also disturbing the electrons and ruining their interference pattern. Thus, it is not possible to know simultaneous both the precise position and the momentum of a microscopic particle, such as an electron or atom. It is the way of nature.

The Uncertainty Principle quantifies the uncertainties of position and momentum as follows [6]:

$$\Delta x \Delta p_x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{1.2}$$

where Δx and Δp_x are the uncertainties associated with these quantities, $\hbar = h/2\pi$. The more precisely something's position is determined, the less precisely its momentum is known. If Δx is very small, Δp_x must be large, and vice versa. The x direction is picked, but it can also be applied for the y or z directions.

1.3 Schrödinger Equation

A particle of matter, such as electron, can be described by a generalized wavefunction ψ, which can determine the all of the measurable quantities of a particle, including its energy E and momentum p. The absolute value of the square of the wavefunction, $|\psi|^2$, is proportional to the probability that the particle occupies a given space at a given time. The Schrödinger equation applied to any confined particle and for motion in one dimension along the x-axis, shown as follows:

$$\frac{d^2\psi}{dx^2} = \frac{-8\pi^2 m}{h^2}(E - V)\psi \tag{1.3}$$

The total energy of a system is the sum of the potential energy (V) and kinetic energy (KE), shown as follows:

$$E = KE + V = \frac{p^2}{2m} + V \tag{1.4}$$

where the KE is equal to $p^2/2m$, V is potential energy, m is the particle mass, p is the momentum.

1.4 Particle in a Potential Box

In order to understand nanotechnology, we must understand atoms, electrons, and photons, which are controlled by quantum mechanism [5, 9].

From the view of "the particle in a box" mode (i.e., a one-dimensional motion of a particle, such as an electron, is restricted between two rigid walls separated by a distance L between the opposite walls of the box) (also known as the infinite potential well or the infinite square well) in quantum mechanics [7], in which we can approximate a particle/wave at the bottom of an infinitely deep, square well. It means no particle can get enough energy to get out the square well, and the wavefunction outside the box must therefore be zero. It follows that the wavefunction inside the box must be zero at the points $x = 0$ and $x = L$. This is called the boundary condition. Therefore, we can expect that the solution to the time-independent wave equation will be of the form of a travelling wave:

$$\psi(x) = A \sin kx = A \sin \frac{2\pi x}{\lambda} \tag{1.5}$$

where $k = 2\pi/\lambda$.

The boundary conditions associated with the walls are satisfied as long as $k = n\pi/L$, or the allowed wavelengths of the electron are $\lambda = 2L/n$ where $n = 1,2,3,\ldots$

$$\psi(x) = N \sin\left(\frac{n\pi x}{L}\right) \tag{1.6}$$

where, $N = 2iA$, A is the amplitude for this wave function, L is the width of the well, x is the distance from one wall, and $n = 1,2,3,\ldots$. This equation gives the allowed wave functions for a particle in an infinitely deep potential well.

This means that the possible values of k are discrete, or quantized. This in turn has the consequence that also the energy levels have to be discrete. The KE, is equal to $p^2/2m$, where $p = h/\lambda$ from the de Broglie relationship and $k = 2\pi/\lambda$. We thus can obtain:

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m\left(\frac{2\pi}{k}\right)^2} = \frac{h^2k^2}{8m\pi^2} \tag{1.7}$$

With the substitution $k = n\pi/L$ this becomes:

$$KE = \frac{n^2h^2}{8mL^2} \tag{1.8}$$

The potential energy, V, is zero within the one-dimensional box, and therefore the total energy, E, equals KE. Thus:

$$E = V + KE = \frac{n^2h^2}{8mL^2} \tag{1.9}$$

Here, $n = 1,2,3,\ldots$. The energy of the particle is quantized. This is what we want to expect about quantum mechanics. It should be pointed out that $n = 0$ is forbidden because this would lead to the wavefunction being zero everywhere. And this status will lead to losing particle. Thus, the particle must have a minimum energy of $E_1 = h^2/8mL^2$ when $n = 1$. This is known as the zero point energy. The next energy level up is $n = 2$, which gives $E_2 = 4h^2/8mL^2 = 4E_1$. Like standing waves, the electrons of an atoms can take on only very specific energies (or wavelengths). Electrons in the highest occupied energy level are called valence electrons. When an electron in an atom drops from one energy state to a lower state, a photon is emitted. Contrarily, a photon will be absorb after the electron jumps from one energy to a higher state. The photon which is regarded as massless chargeless "packlet" of electromagnetic radiation, behaves like a wave and like a particle at the same time. So do electrons.

1.5 Fermi-Dirac Distribution and Fermi Energy

Whether it is metal, semiconductor, or insulator, all materials have free electrons. Insulators have very few electrons, while conductors have many electrons. Semiconductors have electrons falling somewhere in between. These free electrons are not entirely free, however; they are beholden to the same laws as other electrons. The probability that a particular energy level is described by a probability density function $f(E)$. The distribution of energies for $T > 0$ K is given by the Fermi–Dirac distribution function (or called Fermi function) (Figure 1.1):

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1} \tag{1.10}$$

Here, E_F is the Fermi energy, k_B is Boltzmann's constant (1.38×10^{-23} J K^{-1}), and T is the absolute temperature of the solid.

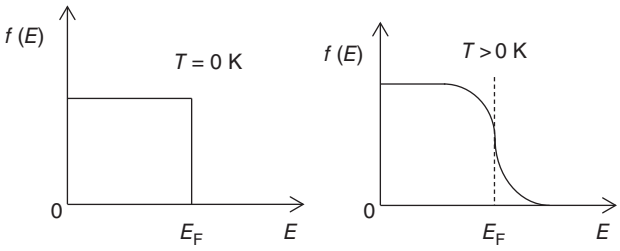

Figure 1.1 The Fermi–Dirac distribution function for a material at $T = 0$ K and at non-zero temperature.

The Fermi level is the highest filled electron level at absolute zero (0 K). The corresponding energy is called Fermi energy E_F, that is, is the energy of the outermost occupied energy level at 0 K, and is simply the top-filled level in the band in a metal and is usually of the order of 5 eV for metals [6]. At temperature above absolute zero, some electrons in levels near to E_F have sufficient thermal energy to be promoted to empty levels above E_F. The Fermi energy is a characteristic of the material and depends upon the concentration of free electrons in the material. In essential, the Fermi energy is the zero-point energy. In the absolute zero temperature ($T = 0$) limit, $f(E) = 1$ for all $E < E_F$, and $f(E) = 0$ for all $E > E_F$. In other words, all electron states below the Fermi energy E_F, are filled, while all those above E_F, all the levels are empty. At non-zero temperature, $f(E)$ describes the fact that some electrons are thermally excited from states just below E_F to states just above E_F. The highest filled electron energy range is called the valence band, while the conduction band is the lowest range of vacant electronic states. Separating the valence and conduction bands is a gap in allowed energies called the band gap. The valence band (VB) and conduction band (CB) are the bands closest to the Fermi level and thus determine the electrical conductivity of the solid. Conductors, semiconductor, and insulators are three solid forms. For a conductor, the conduction bands and valence bands are not separated and there is therefore no energy gap. The conduction band is then partially occupied (even at low temperatures). Insulators are materials with exactly enough electron to keep their energy levels fully occupied. Thus, the valence band of an insulator is completely full and stable. If the band gap of a material between the valence band and the conduction band is sufficiently small, is then called *semiconductors*. However, there is no so called "official" cutoff separating semiconductors from insulators (Figure 1.2). It should point out that E_F for both metals and insulators does not correspond to any physical electron state. It is a theoretical concept and just an energy value that lies between the highest filled state and the next available state [6]. Again, because all materials have at least some free electrons, the probability density function applies to conductors, semiconductors, and insulators. In conductors, the Fermi energy is in the middle of the highest occupied band. In semiconductors and insulators, the Fermi energy is the band gap. The concept of the Fermi energy is a crucially important concept for the understanding of the electrical and thermal properties of solids. Detailed discussion can be found in the physics of electrons in solids book by Tanner [10].

The function $f(E)$ gives the fraction of the allowed levels with energy E which are occupied [11]. It should point out that $f(E)$ is merely a mathematical model;

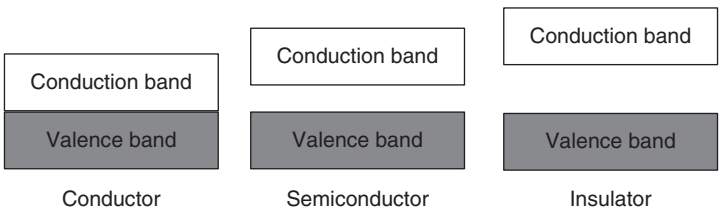

Figure 1.2 The band gap of a conductor, an insulator, and a semiconductor.

and because it is continuous, it indicates that energies inside the band gaps can be occupied by electrons. In reality, energies inside the band gap are forbidden to electrons, due to the discrete electron energies which are separated by the band gaps.

1.6 Density of States

The small size of nanomaterials leads to them unique physical properties. One of the major ways in which nanomaterials differ from corresponding bulk solids in the number of available energy states, due to many of the optical, electronic, and magnetic properties of a nanostructure depend critically on the density of states (DOSs) $g(E)$, represents the number of available states per unit of energy at an energy E [6]. Hence the nanostructured properties of nanomaterials exhibit a strong dependence on dimensionality. For example, in electronic transport the DOS determines the number of states on the number of available states into which they can be scattered. The DOS is not a constant within an energy band. The two-dimensional DOS is a piecewise-continuous approximation to the parabolic three-dimensional DOS in the relationship between DOS and energy, the diverging DOS for one-dimensional quantum wire as the energy approaches that of one of the subband minima, while zero-dimensional quantum dots exhibit "total confinement" discrete DOS function [12]. Further, the distribution of electrons within all the available states varies accompanied with temperature [6]. Detailed knowledge on electronic transport in nanostructures can be found in the quantum mechanics book by Ferry [12]. Optical transitions can occur between the electronic bands if they are allowed by the selection rules. The electronic and vibrational states of nanostructured materials are similar to free molecules and atoms which have discrete energies, thus both the electronic states and the phonon modes have discrete energies, but this is not the case in a solid. Obviously, this continuum of states leads to continuous absorption and emission bands for a solid [13]. The strength of an optical transition is proportional to the joint density states which account for the fact that both the initial and final electron states lie within continuous bands. The energy dependence of the absorption follows the joint DOSs, and therefore exhibits a very different form for nanostructures of different dimensionality [14]. Also the magnetic susceptibility – a dimensionless proportionality constant – the relationship between the magnetization and the applied magnetic field is affected by the DOS. A magnet with a higher DOS at the Fermi level will have more electrons that enter the conduction band. The more electrons in the conduction band, the higher susceptibility for such a magnet, due to the motion of electrons will create magnetic fields [7].

The DOS is a physical property of a material that can be calculated for electrons, photons, or phonons, depending upon the quantum mechanical system. It is commonly symbolized by N and can be given as a function $g(E)$ of either energy E or a function $g(k)$ of the wave vector k. For purely 1D, 2D, and 3D systems, the DOSs are proportional to $E^{(n-2)/2}$ [6].

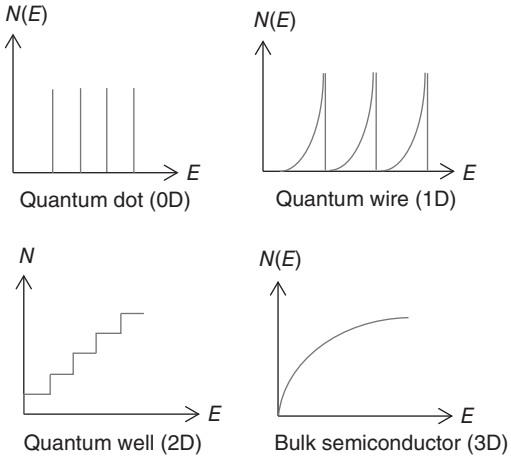

Figure 1.3 DOS plots for 0D (discrete shape), 1D (inverse stepped parabola), 2D (stepped parabola), and 3D (parabolic shape).

The DOSs for 1D system:

$$g(E) = \frac{dN(E)}{dE} = \frac{L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2} E^{-1/2} \tag{1.11}$$

where L is the length of the solid in real space, m is the particular object of mass, $N(E)$ is the total number of states N with an energy less than our selected value of E and is written: $N(E)$, while the DOS $g(E)$ represents the number of available state per unit of energy at an energy E, m is the particle mass, $\hbar$ is Planck's constant $h/2\text{p}$ ($1.0545887 \times 10^{-34}$ J·sec, or 6.582173×10^{-16} eV·sec).

The DOSs for 2D system:

$$g(E) = \frac{dN(E)}{dE} = \frac{Am}{\pi\hbar^2} \tag{1.12}$$

where $A = L^2$ is the area in real space. And the DOS for a 2D solid is a constant.

The DOSs for 3D system:

$$g(E) = \frac{dN(E)}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \tag{1.13}$$

where $V = L^3$, is the volume in real space, E is selected value of energy.

For 0D system (quantum dots), there is no continuous distribution of states and the DOSs takes the form of a spectrum of discrete energy values, which is similar to that found for individual atoms.

The DOSs for zero-dimensional (quantum dots), one-dimensional (quantum wires), and two-dimensional (quantum wells) materials compared to that of a bulk semiconductor material are shown in Figure 1.3. Thus, we can say that bulk materials have enough quantum states, while the nanomateials have fewer quantum states. If we have even fewer quantum states, then we have the structures of the molecules, further on, the atoms [15].

1.7 Quantum Confinement

When the volume of a solid is reduced to the small length in nanoscale system, the energy band structure will be directly affected and the energy levels inside

will become discrete, accordingly, will lead indirectly to changes in the associated atomic structure. The electrons in the reduced-dimensional nanosystem tend to behave more like the description for "particle in a box." Such kind of effect is known as quantum confinement [16, 17]. That means the electronic states are more like those found in localized molecular bonds rather than those in a macroscopic solid.

There are three dimensions to confine, that is, quantum confinement in one dimension-called qauntum wells, quantum confinement in two dimension-called quantum wires, and quantum confinement in three dimension-called quantum dots. It should be confined at least one of these dimensions to less than 100 nm, or even to just a few nanometers, to obtain quantum confinement effect.

The small length scales presenting in nanosystem can not only change the system total energy, but also change the system structure. As the system size decreases, the allowed energy bands become substantially smaller than those in an infinite solid. The electrons in this kind of reduced-dimensional system tend to behave more like the "particle in a box" description in which the energy of different states is dependent on the length of the box. Also as the system size decreases, the chemical reactivity will be changed, which will be a function of the structure and occupation of the outermost electronic energy levels. Accordingly, the physical properties, such as optical, electrical, and magnetic properties, which also depend on the arrangement of the outermost electronic energy levels, will be changed.

The surface is important regardless how large or how small the material is. The surface of a material depends on its size and geometric shape. Both the surface area to volume ratio (S/V) and the specific surface area ($m^2\,g^{-1}$) of a system are inversely proportional to the size of particle and both increase remarkably for particles with the size less than 100 nm in diameter. If an atom is located at a surface then it is clear that the number of nearest-neighbor atoms are reduced, leading to differences in bonding and electronic structure. Obviously, in a nanosystem, a large proportion of the total number of atoms will be on the surface, while a bulk solid material will typically have less than 1% of its atoms on the surface. Thus, more dangling bonds will be present in the nanosystem, giving rise to more reactive active sites, because only the surface of an object is exposed to the reaction and participates in the chemical and physical processes. Therefore, such a reduced-dimensional nanosystem can be expected to have different physical and chemical properties compared with the bulk solid.

If one dimension is reduced to the nanoscale range (i.e., one-dimensional confinement, 1D confinement) while the other two dimensions remain large, we generate a structure known as a "quantum well." A quantum well is a three-dimensional structure in which two dimensions are large, a third is in the nanoscale range. If two dimensions are reduced to the nanoscale range and the other one dimension remains large (i.e., 2D confinement), the resulting structure is called a "quantum wire." Nanotubes and other nanoscale wires can be quantum wires. When all three dimensions are reduced to the nanoscale range (i.e., 3D confinement) and quantum effects are observed, the resulting structure is termed as "quantum dot." Because quantum wells and quantum wires each have at least one dimension in which the electrons are free to move,

these structures are said to exhibit "partial confinement." However, quantum dots exhibit "total confinement."

1.8 Top-Down and Bottom-Up Approaches to Construct Nanostructures

Nanostructures can be fabricated in numerous ways, however, they can be divided into two broad categories, that is, the bottom-up approach and the top-down approach. The top-down approach to fabricate nanostructures is extremely powerful and can generate effectively microscale objects, involving the removal or reformation of atoms to create the desired structures. In the top-down approach, we remove bulk material from one or more of the three dimensions (length, width, height) of a larger solid, or cut bulk material to fabricate the desired nanostructures with the appropriate properties. In the bottom-up approach, we build low-volume structures by utilizing growth and self-assembly to construct nanostructures from atomic and molecular precursors, even nanoparticles themselves used as the building blocks for the generation of complex nanostructures. We can also design properties and functionalities of the nanostructured solid system by adjusting the size of the building blocks and controlling their self-assembly processes. This approach is essentially highly controlled chemical synthesis processes. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures. When structures fall into nanoscale, there is little choice for a top-down approach, because all of the tools from top-down approaches we have possessed are too big to deal with such tiny objects [2]. Chemical synthesis may be carried out in either the solid, liquid or gaseous state. More generally, liquid phase chemical synthesis involves the reaction of solution of precursor chemicals in either an aqueous or nor-aqueous solvent. Both of these methods can produce a structure small enough for quantum behavior to manifest. The bottom-up approach to fabricate nanostructures at the atomic and molecular scale is the original vision of Richard Feynman, possibly using self-assembly methods. Self-assembly can provide an effective spontaneous pathway for constructing desired three-dimensional new materials whose structure at all levels of construction, from the nanoscale to the macroscopic form [18].

It is regarded as the nanostructures synthesized by the bottom-up approach usually have less defects, more homogeneous chemical composition, and better short and long range ordering, which is driven mainly by the reduction of Gibbs free energy, so that nanostructures are the products in a state closer to a thermodynamic equilibrium state. By contraries, the top-down approach most likely introduced internal stress, besides surface defects and contaminations [2].

In order to exploit new applications, and understand the novel physical properties and phenomena of nanostructures, we must develop the ability for constructing nanostructures first. Many technologies have been explored to fabricate nanostructures.

A major challenge of nanoscience and nanotechnology is to integrate the top-down solid-state physics ways of fabricating structures and the bottom-up

molecular-chemical methods of synthesizing structures, and develop various strategies to reliably construct complex systems over all of the length scales ranging from the molecular systems to the macroscopic systems that can interface with people [19].

For nanotechnology, the central problem is not only to obtain new structure and composition of material, but also to arrange and integrate building blocks into new structures with new form and scale, which constructs new materials with new properties, functions and novel applications. It is key to known which size and shape a material must have for it to possess a particular property, function and application, and to design and to construct nanostructures with desired length scale and shape.

1.9 Nanostructured Materials Based on Dimension

According to the form of products, we can group the nanostructures as follows: (i) zero-dimensional (0D) nanstructures, such as nanoparticles and quantum dots, synthesized by colloidal processing, and so on, (ii) one-dimensional (1D) nanostructures, such as nanorods, nanofibers, nanowires, nanotubes, and nanoribbons, synthesized by template-based electroplating techniques, chemical vapor deposition (CVD) method, and so on, (iii) two-dimensional (2D) nanostructures, such as graphene or graphene oxide nanosheets, synthesized by the CVD method, or oxidation methods, and so on, (iv) three-dimensional (3D) nanostructures synthesized by self-assembly of nanosized building blocks.

It is well known that nanostructured materials have different types ranging from zero-dimensional quantum dots to one-dimensional quantum wires, two-dimensional quantum well, three-dimensional complex nanostructures which comprise of low-dimensional building blocks, where at least in one dimension, there is spatial quantum confinement facilitating size-dependent electronic properties [20].

1.10 Zero-Dimensional Nanostructures

In the 1980s, two major breakthroughs initiated the boom period of nanotechnology. One landmark event is the discover of carbon fullerene C_{60}, which is reported by Sir Harold W. Kroto at the University of Sussex, Richard E. Smalley and Robert Floyd Curl, Jr. at the Rice University in 1985, who were together awarded the 1996 Nobel Prize in Chemistry [21]. Another landmark event is the invention of scanning tunneling microscope in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory, who together won the 1986 Nobel Prize in Physics. Dr. John E. Kelly III, IBM, Senior Vice President, Cognitive Solutions and IBM Research, evaluated this event that, "This invention gave scientists the ability to image, measure and manipulate atoms for the first time, and opened new avenues for information technology that we are still pursuing today."

C_{60} is an isolated molecule made up of 60 carbon atoms, connected together as 60 apexes and 32 faces, among them 20 hexagonal and 12 pentagonal faces,

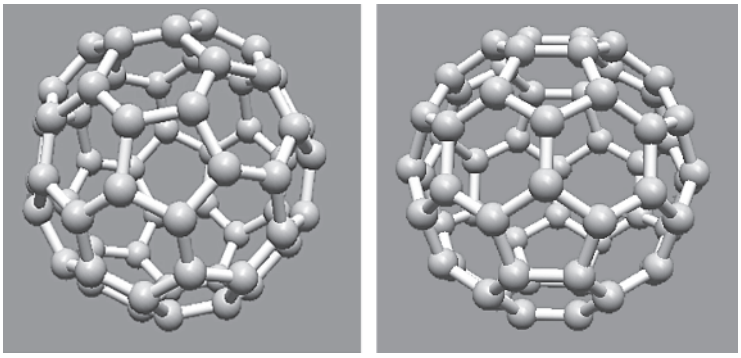

Figure 1.4 C_{60} structure with different views.

symmetrically arrayed to form a molecular ball, similar to a soccer ball. Every pentagon is surrounded by five hexagons. Each carbon atom is bonded to three other carbon atoms by sp^2 hybrid orbital (Figure 1.4). However, because of the curvature of the surface there is about 10% sp^3 character [22].

C_{60} is an extremely stable molecule with the diameter of 7.10 Å (0.710 nm) [21], in the kinetic sense, with a carbon atom placed at each of the 60 vertices of the structure, but it is not a stable molecule in the thermodynamic sense due to extreme bond strain, which is regarded as the first zero-dimensional nanoarchitecture [2]. Since it is very stable and does not require additional atoms for the C_{60} molecule to satisfy chemical bonding requirements, it is expected to own low surface energy. C_{60} has some unique properties, such as superconductivity [23], non-linear optical properties [24], reversible redox behavior [25], magnetism [26], and so on.

Beside C_{60} and other fullerene molecules, there are many other zero-dimensional nanostructures, such as nanoparticles, nanoclusters, nanocrystals, and quantum dots. 0D nanostructures are the simplest building block that may be used for designing and constructing 1D, 2D, and complex 3D nanostructures, and nanodevices.

Nanoparticles, is the term for particles between 1 and 100 nm in size regardless of size and morphology, which generally comprise all 0D nanoscale building blocks. Nanoclusters usually refer to as those 0D nanostructures with at least one dimension between 1 and 10 nm and a narrow size distribution. Nanocrystals are usually referred to those ultrafine particles with at least one dimension below 100 nm, composed of atoms in either a single- or poly-crystalline arrangement. Quantum dots are often used to define those nanoparticle that the characteristic dimension is sufficiently small and quantum effects can be observed.

Nanoparticles may or may not exhibit size-related properties which are quite different from those observed in fine particles or bulk materials [27]. Nanoparticles have a wide variety of applications, including as catalysts or catalytic supports [28], and building blocks for electronic nanodevices [29] due to their unique electronic properties, as fluorescent biological labels [30], and biomedical imaging [31] in biology and medicine due to their unique optical properties, as waste water

treatment [32] and medical diagnostics and treatments [33] and drug and gene delivery [34] for magnetic nanoparticles, and so on.

1.11 One-Dimensional Nanostructures

Carbon nanotubes were discovered by Sumio Iijima of NEC Laboratory in Japan in 1991 [35]. In 1993, Iijima and Ichihashi at NEC Laboratory, and Donald Bethune of the IBM Almaden Research Center in California, independently discovered single-walled carbon nanotubes (SWCN) in 1993 [36, 37]. The individual single-walled carbon nanotubes have very small diameter, typically ~1 nm in diameter, and are curled and looped rather than straight (Figure 1.5) [38]. A SWCN is defined by a cylindrical graphene sheet with a diameter of about 0.7–10.0 nm, though most of the observed SWCNs have diameters <2 nm [39]. SWCNs are called quasi-one-dimensional quantum structures, or pseudoquantum wires if we neglect the two ends of a carbon nanotube and focus on the large aspect ratio of the cylinder. Carbon nanotubes have been demonstrated that they present metallic or semiconducting properties depending upon their precise structure and diameter [38]. Carbon nanotubes have great impact in nanoscience and nanotechnology, due to their unusual electronic, optical, magnetic, mechanical properties, as well as extraordinary thermal conductivity making them idea building blocks for a wide range of applications. For instance, carbon nanotubes find applications as additives to various structural materials [40], near-field microscopic probes [41], field emission-based devices [42], chemical sensor [43], catalyst support [44], hydrogen storage [45], biosensors [46], supercapacitors [47], and so on.

Besides carbon nanotubes, there are other one-dimensional nanostructures, which have been called by a variety of names, including nanofibers, nanowires, nanorods. Usually, the nanowires have a high aspect ratio than that of nanorods. A great challenge with nanowires is to construct functional architectures with

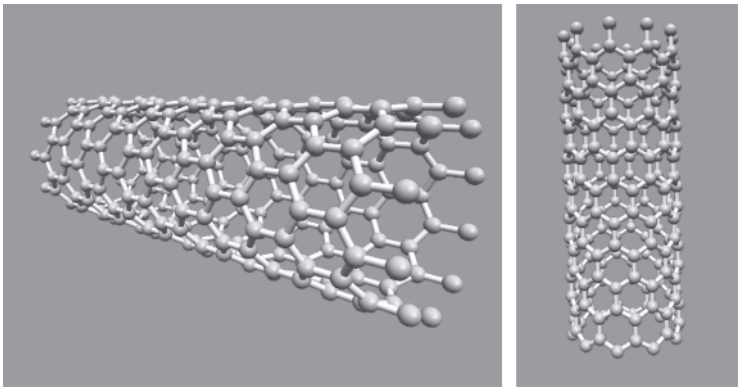

Figure 1.5 Carbon nanotubes with different views.

exceedingly high densities of nanowires, which is the basis for the development of nanoscale electronic, optoelectronic and photonic circuitry.

1.12 Two-Dimensional Nanostructures

The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene" [48]. A one-atom-thick planar sheet of sp^2 hybrid bonded carbon atoms arranged in hexagon structure with 120° C—C bond angle, that is, a monolayer of graphite is called graphene. Each carbon atom has three nearest-neighbor carbon in the layer (Figure 1.6). This is a typical 2D nanostructure. These carbon atoms are densely packed in a honeycomb crystal lattice within a graphene sheet. Usually, graphene can be classified as monolayer graphene, bilayer graphene, and few-layer graphene ($3 < \text{layer number} < 10$). The carbon–carbon bond length in graphene is about 0.142 nm. The interplane distance between two adjacent graphene layers in AB stacked graphite is 0.335 nm [49].

Graphene displays a metallic (zero-gap) character. However, as the Fermi surface is of zero dimension, the term semi-metal or zero-gap semiconductor is appropriate [50]. Graphene exhibits the quantum Hall effect at room temperature [51], extremely high electron/hole mobility (>200,000 $cm^2\ V^{-1}\ s^{-1}$ at room temperature) [52], and high thermal conductivity.

These unique properties of graphene nanosheets making them a wide range of applications. For instance, graphene find applications as a thin flexible ultra-strong film and extremely good conductor applied in flexible electronics due to the high thermal and electrical conductivities, the transparent, elastic, chemically inert, and stable character for graphene nanosheets [53], graphene

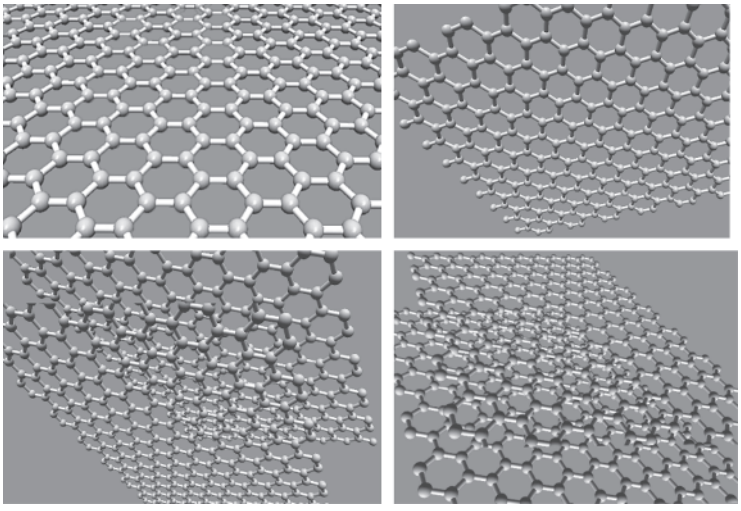

Figure 1.6 Single-layer and di-layer graphene nanostructures with different views.

transistors for high-frequency electronics [54], future ultrafast operation in optoelectronic technologies due to its tunable optical properties, broadband absorption ranging from UV to THz frequencies, and high electrical mobility [55], graphene-based (chemically doped graphene nanoribbons) transistors used in digital logic gates for [56], channel [57], resistive switch [58], storage layer [59] for digital nonvolatile graphene memories, graphene membranes and cantilevers for Mass sensors [60], graphene-based energy applications including supercapacitors [61], lithium ion batteries [62], Ni–MH batteries [63], fuel cells [64], and solar cells [65], and so on.

Two-dimensional nanostructures can be defined as a structure where only one direction is restricted and is comparable to the exciton Bohr radius while the other directions is not restricted, leading to quantum confinement. Thin films are 2D nanostructures. There are many ways to form 2D nanostructures, for instant, evaporation, molecular beam epitaxy, chemical vapor deposition, atomic layer deposition, electrochemical deposition, electroless deposition, spincoating or dip-coating of gel, Langmuire–Blodgett films, and self-assembly monolayers [2, 16].

1.13 Three-Dimensional Nanostructures: Superstructures and Hybrid Structures

Hierarchical nanostructures are three-dimensional materials, which gradually grow from one parent structure into a more complex form [15]. The self-assembly of nanosized building blocks can form 3D architectures [16]. And usually self-assembled aggregates exhibit hierarchical structure. Bio-mimetic self-assembly can not only form clearly defined hierarchical structures with greater strength against external stresses such as mechanical, electric, or magnetic force, but also exhibit higher stability against changes in environment conditions such as pH, temperature, and pressure. It is important that many self-assembly aggregates are strong enough to put up with unit operations and even perform mechanical action under the right conditions. For example, lipid bilayers formed by a self-assembly process have mechanical strength comparable to stainless steel of the same thickness, yet they extremely flexible [18]. This makes the self-assembly 3D structures (Figure 1.7) [66, 67] to find many applications. Self-assembly can form various three-dimensional structures. For instant, spherical micelles, cylindrical rod-like micelles, bilayer sheets, and other bicontinuous or tri-continuous structures can be generated from short chain amphiphilic molecules via strong hydrophobic attraction between hydrocarbon molecules [68].

Nanosized hierarchical structures are good candidates for use in medical applications, environmental greening, and renewable sources of energy [15], such as self-assembly delivery vehicles used as deliver materials of interest on the specific target [69], self-assembly nanoscale components into working electronics used in nanoelectronics [70], superhydrophobic surface [71], photocatalytic agents [72], and so on.

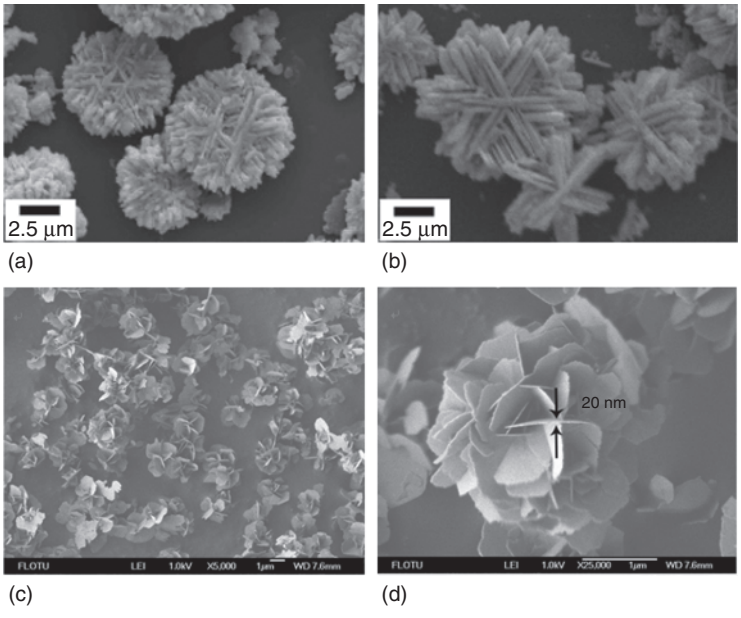

Figure 1.7 (a,b) SEM images of 3D WO_3 nanostructures synthesized by a self-assembly manner (Yin *et al*. 2013 [66]. Reproduced with permission of American Chemical Society.); (c,d) SEM and TEM images of peonylike 3D $Ni(OH)_2$ superstructures, respectively. (Cao *et al*. 2010. [67]. Reproduced with permission from Wiley-VCH Verlag Gmbh & Co. KGaA, Winheim).

An aim of the book is to describe the synthesis methods developed for synthesizing a range of nanoscale building blocks with strictly controlled dimension, size, shape, compositions, and corresponding physical properties, and applications, including optical, electric, magnetic applications, superhydrophobic, optical catalytic, energy-storage (such as lithium ion batteries, Ni–MH batteries, supercapacitors), bioapplications, and so on.

References

1 Feynman, R. (1960) There's Plenty of Room at the Bottom. *Eng. Sci.*, **23** (5), 22–36.
2 Cao, G. (2004) *Nanostructures & Nanomaterials-Synthesis: Properties & Applications*, Imperial College Press.
3 National Research Council (2002) *Small Wonders, Endless Frontiers: Review of the National Nanotechnology Initiative*, National Research Council, National Academy Press, Washington, D.C.
4 Bhushan, B. (ed.) (2006) *Springer Handbook of Nanotechnology*, 2nd edn, Springer-Verlag, Berlin, Heidelberg.
5 Hayward, D.O. (2002) *Quantum Mechanics for Chemists*, The Royal Society of Chemistry.
6 Fischer-Cripps, A.C. (2008) *The Materials Physics Companion*, Taylor & Francis, Group.

7 Rogers, B., Pennathur, S., and Adams, J. (2008) *Nanotechnology: Understanding Small Systems*, CRS Press, Taylor & Francis Group.
8 Rae, A.I.M. (1992) *Quantum Mechanics*, 3rd edn, Institute of Physics, Bristol, England.
9 Heikkilä, T.T. (2013) *The Physics of Nanoelectronics Transport and Fluctuation Phenomena at Low Temperatures*, Oxford University Press, UK.
10 Tanner, B.K. (1995) *Introduction to the Physics of Electrons in Solids*, Cambridge University Press, UK.
11 Cox, P.A. (2005) *The Electronic Structure and Chemistry of Solids*, Oxford University Press.
12 Ferry, D.K. (1997) *Transport in Nanostructures*, Cambridge University Press.
13 Fox, M. (2001) *Optical Properties of Solid*, Oxford University Press.
14 Kelsall, R.W., Hamley, I.W., and Geoghegan, M. (eds) (2005) *Nanoscale Science and Technology*, John Wiley & Sons, Ltd..
15 Hornyak, G.L., Dutta, J., Tibbals, H.F., and Ra, A.K. (eds) (2008) *Introduction to Nanoscience*, CRS Press, Taylor & Francis Group.
16 Fahlman, B.D. (2011) *Materials Chemistry*, 2nd edn, Springer, Netherlands.
17 Yu, P.Y. and Cardona, M. (2001) *Fundamentals of Semiconductors: Physics and Materials Properties*, 3rd edn, Springer-Verlag GmbH & Co. KGaA, Berlin and Heidelberg.
18 Lee, Y.S. (2008) *Self-assembly and Nanotechnology: A Force Balance Approach*, John Wiley & Sons, Inc.
19 Kittel, C. (2005) *Introduction to Solid State Physics*, 8th edn, John Wiley & Sons, Inc.
20 Murugan, A.V. and Vijayamohanan, K. (2007) Applications of nanostructured hybrid materials for supercapacitors, in *Nanomaterials Chemistry: Recent Developments and New Directions* (eds C.N.R. Rao, A. Müller, and A.K. Cheetham), Wiley-VCH Verlag GmbH & Co. KGaA.
21 Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F., and Smalley, R.E. (1985) *Nature*, **318**, 162.
22 Haddon, R.C. (1993) *Science*, **261**, 1545.
23 Suzuki, S., Chida, T., and Nakao, K. (2003) *Adv. Quantum Chem.*, **44**, 535.
24 Brusatin, G. and Signorini, R. (2002) *J. Mater. Chem.*, **12**, 1964.
25 Echegoyen, L. and Echegoyen, L.E. (1998) *Acc. Chem. Res.*, **31**, 593.
26 Arcon, D. and Prassides, K. (2001) *Struct. Bonding*, **100**, 129.
27 Cai, X.C., Anyaogu, K.C., and Neckers, D.C. (2007) *J. Am. Chem. Soc.*, **129**, 11324.
28 Turner, M., Golovko, V.B., Vaughan, O.P.H., Abdulkin, P., Berenguer-Murcia, A., Tikhov, M.S., Johnson, B.F.G., and Lambert, R.M. (2008) *Nature*, **454**, 981.
29 Fan, H., Wright, A., Gabaldon, J., Rodriguez, A., Brinker, C.J., and Jiang, Y.-B. (2006) *Adv. Funct. Mater.*, **16**, 891.
30 Bruchez, M., Moronne, M., Gin, P., Weiss, S., and Alivisatos, A.P. (1998) *Science*, **281**, 2013.
31 Zabow, G., Dodd, S., Moreland, J., and Koretsky, A. (2008) *Nature*, **453**, 1058.
32 Krieg, E., Weissman, H., Shirman, E., Shimoni, E., and Rybtchinski, B. (2011) *Nat. Nanotechnol.*, **6**, 141.

33 Zhang, Y., Jeon, M., Rich, L.J., Hong, H., Geng, J., Zhang, Y., Shi, S., Barnhart, T.E., Alexandridis, P., Huizinga, J.D., Seshadri, M., Cai, W., Kim, C., and Lovell, J.F. (2014) *Nat. Nanotechnol.*, **9**, 631.

34 Davis, M.K., Zuckerman, J.E., Choi, C.H.J., Seligson, D., Tolcher, A., Alabi, C.A., Yen, Y., Heidel, J.D., and Ribas, A. (2010) *Nature*, **464**, 1067.

35 Iijima, S. (1991) *Nature*, **354**, 56.

36 Iijima, S. and Ichihashi, T. (1993) *Nature*, **363**, 603.

37 Bethune, D.S., Kiang, C.H., De Vries, M.S., Gorman, G., Savoy, R., Vasquez, J., and Beyers, R. (1993) *Nature*, **363**, 605.

38 Harris, P.J.F. (1999) *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century*, Cambridge University Press.

39 Saito, R., Dresselhaus, G., and Dresselhaus, M.S. (1998) *Physical Properties of Carbon Nanotubes*, Imperial College Press.

40 Rodriguez, N.M., Chambers, A., and Baker, R.T.K. (1995) *Langmuir*, **11**, 3862.

41 Dai, H., Rinzler, A.G., Nikolaev, P., Thess, A., Colbert, D.T., and Smalley, R.E. (1996) *Chem. Phys. Lett.*, **260**, 471.

42 de Heer, W.A., Châtelain, A., and Ugarte, D. (1995) *Science*, **270**, 1179.

43 Kong, J., Franklin, N.R., Zhou, C., Chapline, M.G., Peng, S., Cho, K., and Dai, H. (2000) *Science*, **287**, 622.

44 Planeix, J.M., Coustel, N., Coq, B., Botrons, B., Kumbhar, P.S., Dutartre, R., Geneste, P., Bernier, P., and Ajayan, P.M. (1994) *J. Am. Chem. Soc.*, **116**, 7935.

45 Darkrim, F.L., Malbrunot, P., and Tartaglia, G.P. (2002) *Int. J. Hydrogen Energy*, **27**, 193.

46 Salvador-Morales, C., Flahaut, E., Sim, E., Sloan, J., Green, M.L.H., and Sim, R.B. (2006) *Mol. Immunol.*, **43**, 193.

47 Frackowiak, E. and Béguin, F. (2002) *Carbon*, **40**, 1775.

48 *Nobel Foundation Announcement in* 2010, www.NobelPrize.org.

49 Haering, R.R. (1958) *Can. J. Phys.*, **36**, 352.

50 Foa Torres, L.E.F., Roche, S., and Charlier, J.-C. (2014) *Introduction to Graphene-based Nanomaterials*, Cambridge University Press.

51 Novoselov, K.S., Jiang, Z., Zhang, Y., Morozov, S.V., Stomer, H.L., Zeitler, U., Mann, J.C., Boebinger, G.S., Kim, P., and Geim, A.K. (2007) *Science*, **315**, 1379.

52 Bolotin, K.I., Sikes, K.J., Jiang, Z., Klima, M., Fudenberg, G., Hone, J., Kim, P., and Stormer, H.L. (2008) *Solid State Commun.*, **146**, 351.

53 Torrisi, F., Hasan, T., Wu, W., Jung, S., Bonaccorso, F., Paul, P.J., Chu, D.P., and Ferrari, A.C. (2012) *ACS Nano*, **6**, 2992.

54 Liao, L., Lin, Y.C., Bao, M.Q., Cheng, R., Bai, J.W., Liu, Y., Qu, Y.Q., Wang, K.L., Huang, Y., and Duan, X.F. (2010) *Nature*, **467**, 305.

55 Mueller, T., Xia, F., and Avouris, P. (2010) *Nat. Photonics*, **4**, 297.

56 Farmer, D.B., Golizadeh-Mojarad, R., Perebeinos, V., Lin, Y.-M., Tulevski, G.S., Tsang, J.C., and Avouris, P. (2009) *Nano Lett.*, **9**, 388.

57 Stützel, E.U., Burghard, M., Kern, K., Traversi, F., Nichele, F., and Sordan, R. (2010) *Small*, **6**, 2822.

58 Wu, C., Li, F., Zhang, Y., and Guo, T. (2012) *Appl. Phys. Lett.*, **100**, 042105.

59 Hong, A.J., Song, E.B., Yu, H.S., Allen, M.J., Kim, J., Fowler, J.D., Wassei, J.K., Park, Y., Wang, Y., Zou, J., Kaner, R.B., Weiller, B.H., and Wang, K.L. (2011) *ACS Nano*, **5**, 7812.

60 Kim, S.Y. and Park, H.S. (2010) *Nanotechnology*, **21**, 105710.

61 Cao, H.Q., Wu, X.M., Yin, G., and Warner, J.H. (2012) *Inorg. Chem.*, **51**, 2954.

62 Li, B.J., Cao, H., Shao, J., and Qu, M.Z. (2011) *Chem. Commun.*, **47**, 10374.

63 Li, B., Cao, H.Q., Shao, J., Zheng, H., Lu, Y.X., Yin, J.F., and Qu, M.Z. (2011) *Chem. Commun.*, **47**, 3159.

64 Luo, B., Liu, S., and Zhi, L. (2012) *Small*, **8**, 630.

65 Yan, X., Cui, X., Li, B., and Li, L.-S. (2010) *Nano Lett.*, **10**, 1869.

66 Yin, J., Cao, H., Zhang, J., Qu, M., and Zhou, Z. (2013) *Cryst. Growth Des.*, **13**, 759.

67 Cao, H., Zheng, H., Liu, K., and Warner, J.H. (2010) *ChemPhysChem*, **11**, 489.

68 Desai, R.C. and Kapral, R. (2009) *Dynamics of Self-organized and Self-assembled Structures*, Cambridge University Press.

69 Katherine Wang, C.H. (2011) *Developing Gene Delivery Vehicles using Self-assembly*, Gradworks.

70 Heath, J.R. and Ratner, M.A. (2003) *Phys. Today*, **56**, 43.

71 Wu, S.S., Yin, S.F., Cao, H.Q., Lu, W.X., Yin, J.F., and Li, B.J. (2011) *J. Mater. Chem.*, **21**, 8734.

72 Cao, H.Q., Xiao, Y.J., Lu, Y.X., Yin, J.F., Li, B.J., Wu, S.S., and Wu, X.M. (2010) *Nano Res.*, **3**, 863.