

Chapter 1

Self-assembled ordering nanomaterials

§ 1.1 Introduction to nanomaterials

Although a broad definition, the term ‘nanomaterials’ generally refers to those materials which have structured components with at least one dimension less than 100 nm. Nanostructures constitute a bridge between molecules and infinite bulk systems. Individual nanostructures include clusters, quantum dots, nanocrystals, nanowires (NWs) and nanotubes, while collections of nanostructures involve arrays, assemblies, and superlattices of the individual nanostructures [1,2]. Table 1.1 lists the typical dimensions of nanomaterials. The uniqueness of the structural characteristics, energetics, response, dynamics, and chemistry of nanostructures constitutes the basis of nanoscience [3]. Suitable control of the properties and response of nanostructures can lead to new devices and technologies, especially potential applications in molecular electronics, ultra-high density data storage, biosensors, and quantum computation devices.

The physical and chemical properties of nanostructures are distinctly different from those of either a single atom (molecule) or of the bulk matter with the same chemical composition. These differences between nanomaterials and their molecular and bulk counterparts are related to the spatial structures and shapes, phase changes, energetics, electronic structure, chemical reactivity, and catalytic properties of large, finite systems, and their assemblies. Therefore, it is possible to process materials which can be tuned via size control to achieve specific functionality.

Table 1.1 Nanostructures and their assemblies from Ref. [3]

Nanostructure	Size	Material
Clusters, nanocrystals quantum dots	Radius, 1-10 nm	Insulators, semiconductors, metals, magnetic materials
Other nanoparticles (NPs)	Radius, 1-100 nm	Ceramic oxides
Nanobiomaterials, Photosynthetic reaction center	Radius, 5-10 nm	Membrane protein
NWs	Diameter, 1-100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	Diameter, 1-100 nm	Carbon, layered Chalcogenides, BN, GaN
Nanobiorods	Diameter, 5 nm	DNA
Two-dimensional (2D) arrays of NPs	Area, several nm ² - μm ²	Metals, semiconductors, magnetic materials
Surface and thin films	Thickness, 1- 100 nm	Insulators, semiconductors, metals, DNA
Three-dimensional (3D) superlattices of NPs	Several nm in three dimensions	Metals, semiconductors, magnetic materials

Size effects are the most essential aspect of nanomaterials. When the dimensions of a system are reduced to the nanoscale domain, the number of atoms at the surface significantly increases, along with the increase in surface area per unit volume.

$$\text{Specific surface area} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3 \rho} = \frac{3}{\rho r} \quad (1.1)$$

where r is the radius of the nanoparticle and ρ is its density. Hence, when the dimensions decrease from μm to nm scale, the specific surface area increases by 3 orders of magnitude [4]. In such a case, a large proportion of the atoms will either be at or near the particle surface [5]. For example, metal nanocrystal of 1 nm diameter

will have ~100% of its atoms on the surface. A nanocrystal of 10 nm diameter on the other hand, would have only 15% of its atoms on the surface [6]. A nanocrystal with a higher surface area would be expected to be more reactive than the same mass of material made up of larger particles, as growth and catalytic chemical reactions normally occur at surfaces. Furthermore, the qualitative change in the electronic structure arising due to quantum confinement in small nanocrystals will also bestow unusual catalytic properties on these particles, which may be very different from those of the bulk metal.

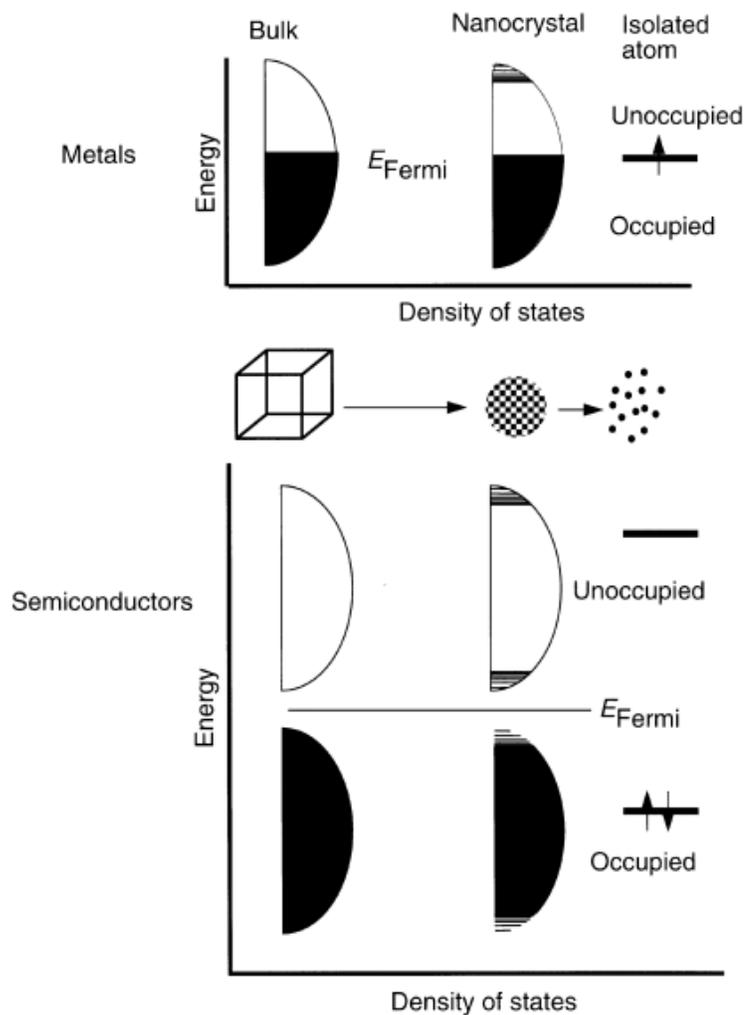


Figure 1.1 Density of states for metal and semiconductor nanocrystals compared to those of the bulk and of isolated atoms (reproduced from [6]).

There are two types of size effects: one is concerned with specific size effects (*e.g.* magic numbers of atoms in metal clusters, quantum mechanical effects at small sizes) and the other with size-scaling applicable to relatively larger nanostructures. The former includes the appearance of new features in the electronic structure. Figure 1.1 shows how the electronic structures of metal and semiconductor nanocrystals differ from those of bulk materials and isolated atoms. For small particles, the electronic energy levels are not continuous as in bulk materials, but discrete, due to the confinement of the electron wavefunction because of the physical dimensions of the particles.

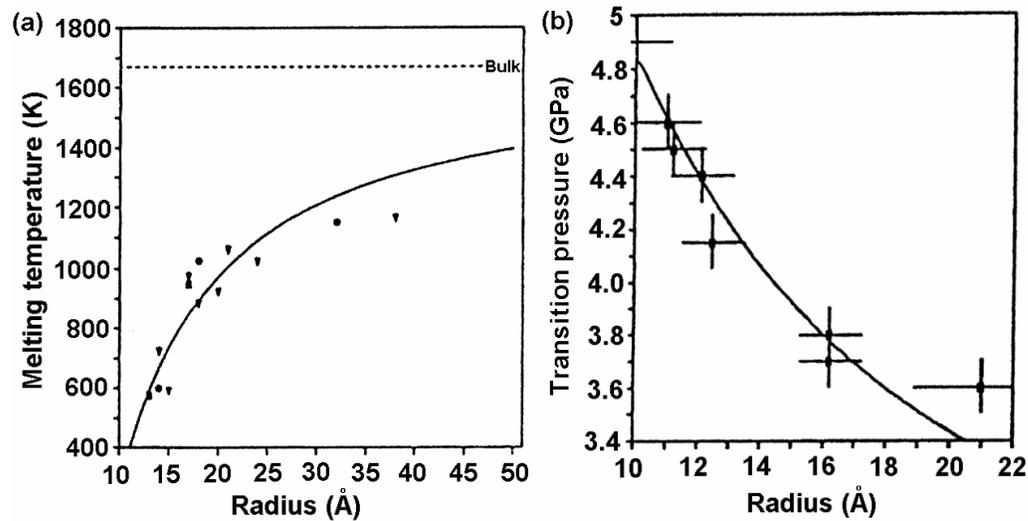


Figure 1.2 Size dependence of the (a) melting temperature of CdS nanocrystals and (b) the pressure induced transformation of wurtzite-rock salt transformation in CdSe nanocrystals (reproduced from [7]).

The intrinsic properties of the interior of nanocrystals, such as melting point, electronic absorption spectra, and other properties, are also affected by size. In a wide variety of materials, ranging from metals to semiconductors to insulators, a decrease in solid-to-liquid transition temperature has been observed with decreasing nanocrystal size [8,9,10]. An example is presented in Figure 1.2(a) for experiments performed on CdS nanocrystals [11]. Melting point depressions of over 50% are

observed for sufficiently small sized nanocrystals. In addition, as the nanocrystals decrease in size, the pressure required to induce transformation to the denser phase increases (Figure 1.2(b), for CdSe), with a scaling law similar to the one that applies to melting, but opposite in direction.

“There’s plenty of room at the bottom”, the 1959 dream statement [12] of the legendary Richard Feynman has been realized in less than half a century by consistent efforts and significant contributions from the scientific community across the globe. Progress made in the past few decades has proven the nature of matter as a whole, and the ability to achieve exciting technological advancement for the benefit of mankind. From the invention of carbon fullerene structures, carbon nanotubes by Iijima and the equally important discovery of inorganic fullerene structures by Tenne, there have been numerous reports [13,14,15,16,17,18] that have discussed the fundamental and technological importance of novel nanostructured materials. Due to lack of space, it is impossible to present a comprehensive overview of all areas of research that may be classified under the ‘nanostructured materials’ banner. Therefore, the choice of topics has been restricted to those of relevance to this thesis, *i.e.* the most significant advances in the synthesis and the understanding of recent development about self-organized or self-assembled nanostructures over the past decade.

§ 1.2 Fundamental aspects of self-assembled nanomaterials

Self-assembly is an incredibly powerful concept in modern molecular science. The ability of carefully designed building blocks to spontaneously assemble into complex nanostructures underpins developments in a wide range of technologies — ranging from materials science through to molecular biology. Due to the multi-disciplinary nature of this new subject, the definition of a self-assembling process may be different among researchers from different fields. Generally speaking, self-assembly is a process in which components, either separately or linked, spontaneously form ordered aggregates [19]. The interactions involved usually are non-covalent, such as electrostatic interactions, hydrogen bonds, van der Waals’

forces, coordination interactions and solvophobic effects [20]. In self-assembled structures, these intermolecular forces connect the molecular building blocks in a reversible, controllable and specific way. Of particular value are the possibilities offered by self-assembly to generate nanoscale complexity with relatively little synthetic input. Furthermore, the ability of assembled superstructures to behave as more than the sum of their individual parts, and exhibit completely new types of behaviour, is of special interest [21].

Self-assembly is scientifically interesting and technologically important for the following reasons [19]:

1. Self-assembly is centrally important in life. For instance, the cell contains an astonishing range of complex structures such as lipid membranes, folded proteins, structured nucleic acids, protein aggregates, molecular machines, and many others that form by self-assembly [22].
2. Self-assembly provides routes to a range of materials with regular structures, such as molecular crystals [23], liquid crystals [24], and semicrystalline and phase-separated polymers [25].
3. Self-assembly occurs widely in systems of components larger than molecules, and there is great potential for its use in materials and condensed matter science [26].
4. Self-assembly seems to offer one of the most general strategies now available for generating nanostructures [27].

Thus, self-assembly is important in a range of fields: chemistry, physics, biology, materials science, nanoscience and manufacturing. There is an exciting opportunity for self-assembly to develop through the interchange of concepts and techniques among these fields.

§ 1.2.1 The principles of self-assembly

§ 1.2.1.1 Components

A self-assembling system consists of a group of molecules or segments of a macromolecule that interact with one another. These molecules or molecular segments may be the same or different. Their interaction leads from some less ordered state (a solution, disordered aggregate or random coil) to a final state (a crystal or folded macromolecule) that is more ordered.

§ 1.2.1.2 Interactions

Self-assembly occurs when molecules interact with one another through a balance of intermolecular forces. These interactions are generally weak (that is, comparable to thermal energies) and non-covalent (van der Waals, electrostatic, hydrophobic interactions, and hydrogen bonds), but relatively weak covalent bonds (coordination bonds) may also play a part [28,29]. However, the internal interaction of the elements does not uniquely define the final state of a self-organizing system. In the self-assembly of larger components (meso- or macroscopic objects), interactions can often be selected and tailored by external forces and geometrical constraints, such as gravitational attraction (*e.g.* particles settling out of suspensions), external electromagnetic fields, and magnetic, capillary, and entropic interactions, which can change the outcome of a self-assembly process, and provide flexibility to process designer.

§ 1.2.1.3 Adjustability

For self-assembly to generate ordered structures, the association must allow the components to adjust their position within an aggregate once it has formed. Therefore, the strength of the bonds between the components must be comparable to

the forces tending to disrupt them. For molecules, the forces are generated by thermal motion. If components stick together irreversibly when they collide, they form a glass rather than a crystal or other regular structure. Self-assembly requires that the components either equilibrate between aggregated and non-aggregated states, or adjust their positions relative to one another once in an aggregate.

§ 1.2.1.4 Environment

The self-assembly of molecules is normally carried out in solution or at a smooth interface, since this allows the required motion of the components. The environment can modify the interactions between the components. The interaction of the components with their environment can strongly influence the course of the process. Moreover, the use of boundaries and other templates in self-assembly is particularly important, because templates can reduce defects and control structures.

§ 1.2.1.5 Mass transport and agitation

For self-assembly to occur, the molecules must be mobile. In solution, thermal motion provides the major part of the motion required to bring the molecules into contact. Self-assembly often operates under equilibrium control. Thus, a growing structure can reorganize during assembly to maximize complementary surface contacts. The final structure thus represents the thermodynamic minimum for a particular collection of atoms with a given connectivity.

§ 1.2.2 Types of self-assembly

There are two main kinds of self-assembly: static and dynamic [30]. Static self-assembly (S) (Table 1.2 and Figure 1.3) involves systems that are at global or local equilibrium and do not dissipate energy. For example, molecular crystals [31,32] are formed by static self-assembly; so are most folded, globular proteins. In

static self-assembly, formation of the ordered structure may require energy (for example in the form of stirring), but once it is formed, it is stable. Most research in self-assembly has focused on this static type.

Table 1.2 Examples of self-assembly (S: static, D: dynamic, T: templated, B: biological).

System	Type	Applications/importance	References
Atomic, ionic, and molecular crystals	S	Materials, optoelectronics	[32,33]
Phase-separated and ionic layered polymers	S		[25]
Self-assembled monolayers (SAMs)	S, T	Microfabrication, sensors, nanoelectronics	[34]
Liquid bilayers and black lipid films	S	Biomembranes, emulsions	[35]
Liquid crystals	S	Displays	[36]
Colloidal crystals	S	Band gap materials, molecular sieves	[37,38]
Bubble rafts	S	Models of crack propagation	[39]
Macro- and mesoscopic structures (MESA)	S or D, T	Electronic circuits	[40,41]
Fluidic self-assembly	S, T	Microfabrication	[42]
'Light matter'	D, T		[43]
Oscillating and reaction-diffusion reactions	D	Biological oscillations	[44]
Bacterial colonies	D, B		[45]
Swarms (ants) and schools (fish)	D, B	New models for computation/optimization	[46,47]
Weather patterns	D		[33]
Solar systems	D		
Galaxies	D		

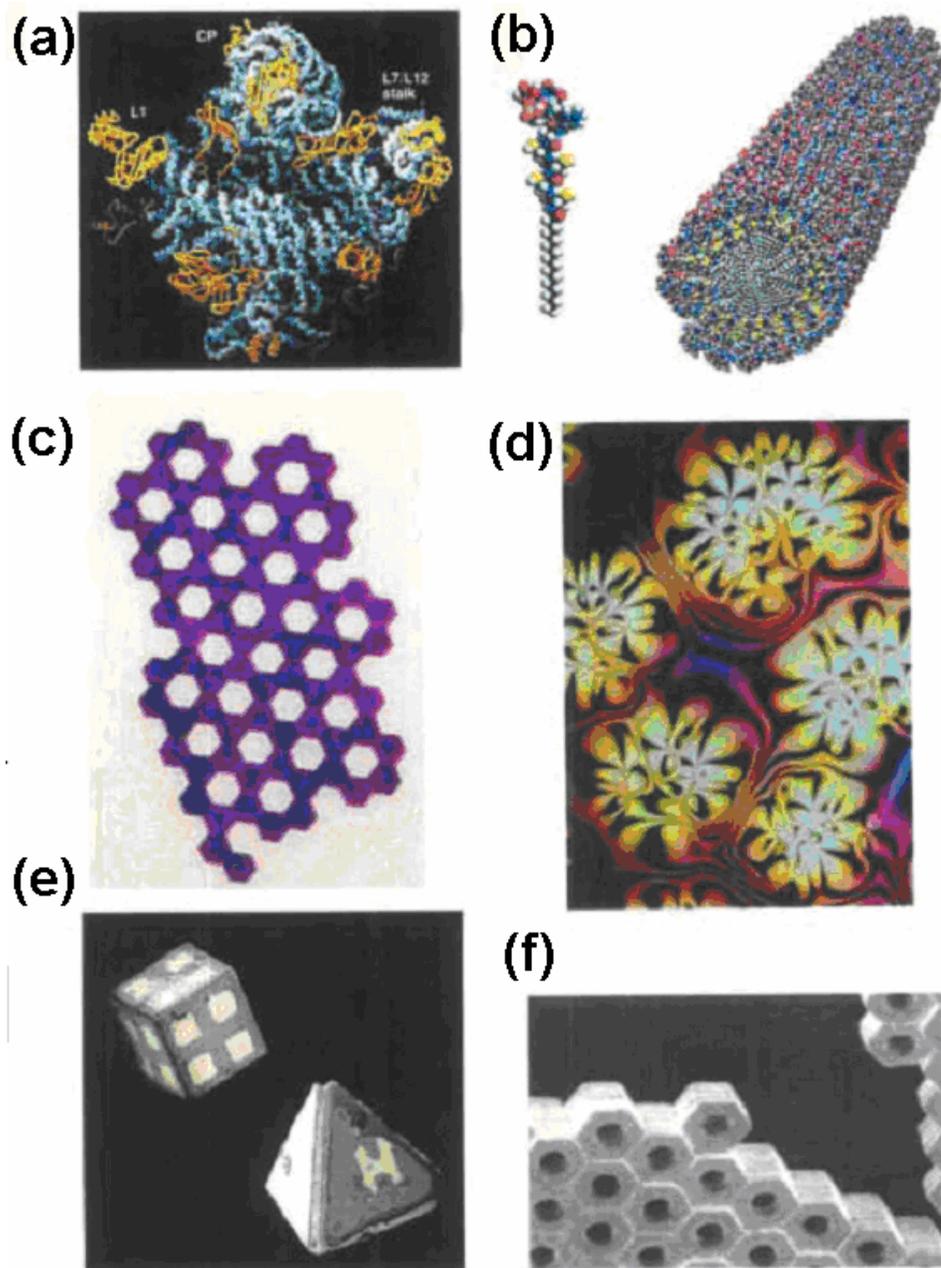


Figure 1.3 Examples of static self-assembly. (a) Crystal structure of a ribosome [48]. (b) Self-assembled peptide-amphiphile nanofibres [49]. (c) An array of millimetre-sized polymeric plates assembled at a water/perfluorodecalin interface by capillary interactions [50]. (d) Thin film of a nematic liquid crystal on an isotropic substrate [51]. (e) Micrometer-sized metallic polyhedra folded from planar substrates [52]. (f) A 3D aggregate of micrometre plates assembled by capillary forces [53].

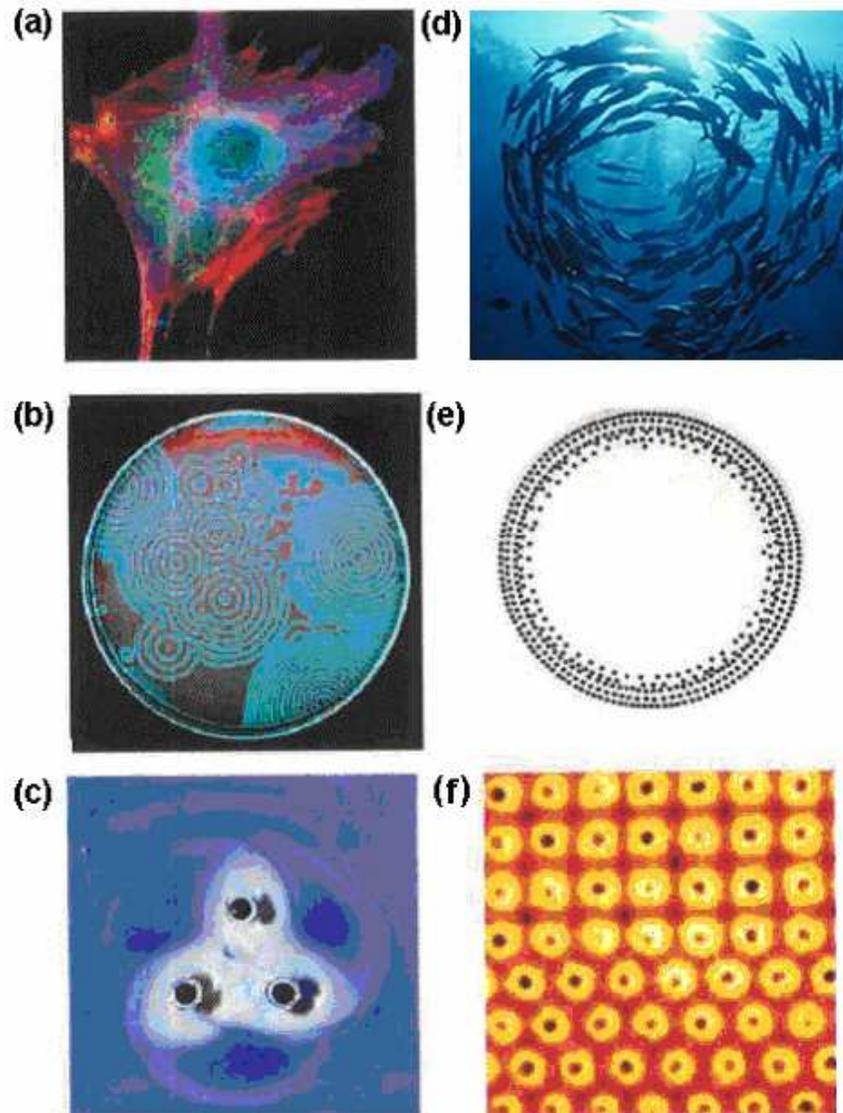


Figure 1.4 Examples of dynamic self-assembly [54]. (a) An optical micrograph of a cell with fluorescently labelled cytoskeleton and nucleus; microtubules (~ 24 nm in diameter) are coloured red. (b) Reaction-diffusion waves in a Belousov-Zhabotinski reaction in a 3.5-inch Petri dish [50]. (c) A simple aggregate of three millimetre-sized, rotating magnetized disks interacting with one another via vortex-vortex interactions [55]. (d) A school of fish. (e) Concentric rings formed by charged metallic beads 1 mm in diameter rolling in circular paths on a dielectric support. (f) Convection cells formed above a micropatterned metallic support. The distance between the centres of the cells is ~ 2 mm.

In dynamic self-assembly (D) (Table 1.2 and Figure 1.4), the interactions responsible for the formation of structures or patterns between components only occur if the system is dissipating energy. The patterns formed by competition between reaction and diffusion in oscillating chemical reactions [44,56] are simple examples; biological cells are much more complex ones. The study of dynamic self-assembly is only in its infancy.

Two further variants of self-assembly are defined by Whitesides and co-worker [30]. In templated self-assembly (T), interactions between the components and regular features in their environment determine the final self-assembly structures. Crystallization on surfaces that determine the morphology of the crystal is one example [34,38]; crystallization of colloids in 3D optical fields is another [43]. The characteristic of biological self-assembly (B) is the variety and complexity of the functions that it produces.

§ 1.3 Current development and applications of self-assembly

§ 1.3.1 Self-assembled monolayers on solid substrates

A self-assembled monolayer (SAM) is a monolayer of organic molecules that forms spontaneously as an ordered lattice on the surface of an appropriate substrate [57]. The molecules in the SAM lattice will chemically bind to the substrate at one end (head group). The other end of the molecules (tail group) constitutes the exposed surface of the SAM. A variety of SAMs have been obtained in the past, for example, thiols form SAMs on metals such as gold [58], silver, copper, iron [59], platinum [60] and palladium [61]. They can also form on some compound semiconductors, such as InP and GaAs [62]. SAMs containing surface-active groups have shown to promote heterogeneous nucleation by reducing the free energy of formation of the crystalline phase [63,64]. Figure 1.5 shows a scanning tunnelling microscope (STM) image of octanethiol molecules forming a SAM on an atomically flat gold substrate [65].

Self-assembly allows for the precise positioning of SAMs. This characteristic

of SAMs makes them good candidates for molecular electronic devices. Today, in most molecular electronic architectures, a SAM is allowed to self-assemble onto the correct location in the device structures. By designing and positioning the proper molecules in the device, the desired functionality is obtained. SAMs have been used as molecular memories [66], molecular wires [67], and have exhibited negative differential resistance [68].

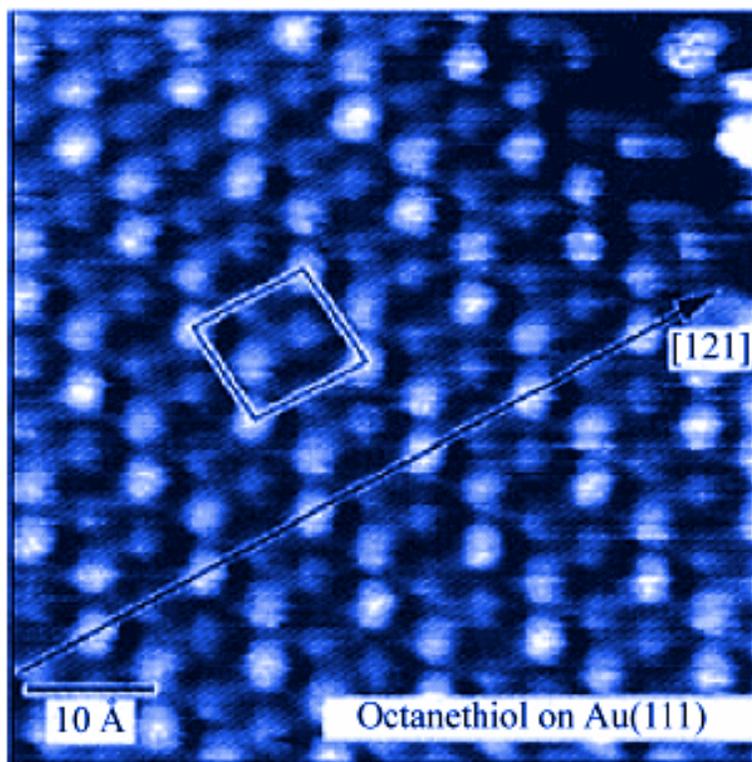


Figure 1.5 Scanning tunnelling microscopy image of octanethiol monolayer on Au (111). The molecules self-assemble on the gold surface and form the observed ordered lattice spontaneously. Octanethiol molecules commensurate with the underlying gold lattice structure as marked in the image (reproduced from [65]).

Using SAMs to build electronic devices and perhaps eventually circuits is an intriguing prospect. They can potentially provide the basis for very high-density data storage and high-speed devices. It is also interesting to investigate the electro-optical properties of molecular devices. Many organic molecules have signature optical

responses especially in the infrared region. It would be beneficial to take advantage of these to make optoelectronic devices [69].

§ 1.3.2 Colloidal self-assembly

Many methods have been developed to process different kinds of colloidal nanocrystals via self-assembly. The reduction of metal ions in solution is the most popular and economical method, although evaporation of metals at high temperature can also yield metal nanoclusters. For example, gold nanocrystals can be prepared either by an aerosol method or a chemistry method. The chemistry route dates back to Faraday in 1857 [70], who first reduced an aqueous gold salt with phosphorus in carbon disulfide and obtained a ruby coloured aqueous solution of dispersed gold NPs. In the aerosol method, gold atoms are evaporated from a carbon crucible in a resistively-heated carbon tube [71,72]. The atoms are entrained in He and induced to condense into nanoclusters by mixing the hot flow from the oven with a room temperature stream of helium. The clusters are molten and recrystallised while still in the gas phase. In order to ensure that all of the clusters are single crystalline, a dilute aerosol stream of clusters suspended in inert gas is passed through a 1 m-long tube in which the clusters are first heated above their melting temperature and then cooled to room temperature. Treating small gold clusters in this way transforms them into face-centred-cubic (fcc) single crystals.

The self-assembly of metal oxides, such as ZnO, CuO, or TiO₂ spheres into ordered arrays with diameters ranging from a 100 nm to a few microns, has also been extensively studied, as a means to fabricate photonic bandgap crystals [73]. These colloidal photonic band gap crystals can be used in lasers [74] and waveguides [75]. Under the influence of capillary forces, the spheres can be packed and made into ordered lattices [76,77]. Such packing processes are controllable by gravity, convection, changing the surface chemistry of the spheres, or imposing geometrical constraints on the system. For example, by assembling a lattice of spheres inside a microchannel, it is possible to fabricate lines and 3-D patterns with internal feature sizes smaller than is allowed by photolithography [78,79]. The space between the spheres can be filled with other materials such as carbon, CdSe, and metal oxides

[80,81]. The filling process can be accomplished by sintering nanocrystals, electrodeposition, chemical vapour deposition, or oxide reduction. It is also possible to remove the spheres after the refill process and produce a porous structure with nano-scale ordered voids [82].

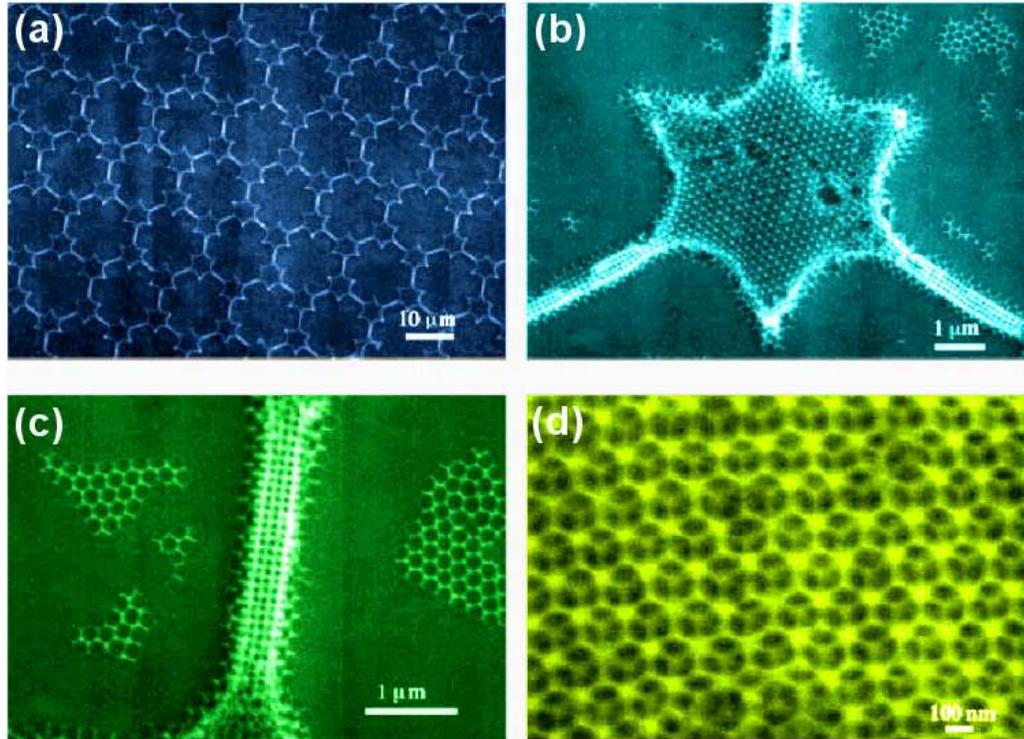


Figure 1.6 Scanning electron microscopy (SEM) images of hierarchical colloidal self-assembly. (a) The largest pattern in the structure is made by using micro-channels. (b) Latex micro-spheres self-assemble in the channels to form a 3D lattice structure. A close up is shown in (c). (d) The spacings between the silica spheres are filled with a porous oxide and then the spheres are removed from the structure (reproduced from [83]).

Figure 1.6 shows examples of a hierarchical self-assembly process that uses porous oxide as the filling material between spheres [83]. In this case, the self-assembly process allows the controlled formation of ordered patterns over three orders of magnitude of length scale. The diameter of the pores in the metal oxide

used to infiltrate the lattices is of the order of 10 nm. The ordered pores in the metal oxide result from mixing the precursor for the metal oxide with a block copolymer and subsequently removing the polymer phase. The porous metal oxide fills the space between a self-assembled lattice of spheres about 100 nm in diameter. It is noteworthy that hierarchical self-assembly can controllably create shapes with nano-scale features in the desired locations, making these features possess great potential applications.

§ 1.3.3 Epitaxially grown self-organized solid-state quantum dots

Molecular beam epitaxy (MBE) and metal-organic vapour phase epitaxy (MOVPE) can produce 2D planes of semiconductors with atomic scale precision. These techniques can also be employed to form quantum dots on semiconductor surfaces by relying on the lattice mismatch between alternative layers [84]. In this growth mode, a thin layer of material (typically a few nanometres) grows epitaxially on a substrate with a different lattice constant. The resultant strain in the deposited layer can initiate a self-organization and convert the continuous overlayer into a group of quantum dots. Si/SiGe and (InGa)As/GaAs are the two most widely-studied material systems for the self-organized growth of quantum dots using this method. The dot diameter ranges from ten to a few hundred nanometres, with typical dot heights below ten nanometres.

The self-assembly of the dots on the surface [85,86] can be tuned by varying the substrate temperature, the substrate angle, the flux ratios, the lattice mismatch, and the growth rate. This has allowed close control of the dot size and distribution and also the average spacing between adjacent dots, forming long range ordered lattices. Patterned substrates with step edges, grooves, and stress concentration locations have been used to guide the growth of the dots [87].

§ 1.3.4 Self-assembly of nanocrystals and nanowires

In nanocrystal self-assembled structures, each individual nanocrystal is the fundamental building unit, and it serves as an ‘artificial atom’ for constructing the ordered structure. Size and shape-controlled nanocrystals can be viewed as molecular matter with a specific shape and electronic structure, and self-assembly of the nanocrystals can form ‘nanocrystal solids’ with orientational order [88]. The interest in individual nanocrystals and NWs is driven toward an understanding of the size- and shape-dependent properties of various materials, and the collective properties of assemblies [89,90].

To date, a diverse range of shapes, sizes and consequently, new material properties are accessible using chemistry methods such as hydrothermal method, soft-template and use of various surfactants. Figure 1.7 shows various nano-objects, even highly asymmetric shapes such as teardrops and tetrapods [91]. Remarkable linear chains of aggregated BaSO₄ or BaCrO₄ NPs [92] can be formed spontaneously in a microemulsion reaction media (Figure 1.8). The colloidal chains are 50 to 500 nm in length and consist of uniform-sized rectangular prismatic crystals (16×6.8×6 nm) spaced at regular intervals of 2 nm and preferentially aligned with the long axis of each particle perpendicular to the chain direction. Formation of the linear array depends on the uniformity in NP size and shape anisotropy, which facilitates crystal-face-specific interactions between the hydrophobic tails of surface-adsorbed surfactant molecules.

The prevalence of self-assembled structures in biological systems has inspired researchers to borrow biological concepts when fashioning new approaches to fabricating self-assembled arrays of nanostructures. Alivisatos and Mirkin [93,94] have modified gold nanocrystals with complementary strands of DNA. When mixed together, the gold nanocrystals recognize each other using the specific biochemistry of DNA to form mixtures of dimer (two nanocrystals) and trimer (three nanocrystals) aggregates. Belcher and co-workers [95,96] have reported the formation of a liquid crystalline phase of virus material, where each virus has a semiconductor nanocrystal tethered at one of its ends. The observation of liquid crystalline behaviour provides a

demonstration of new material properties emerging at the interface between the materials and biological sciences.

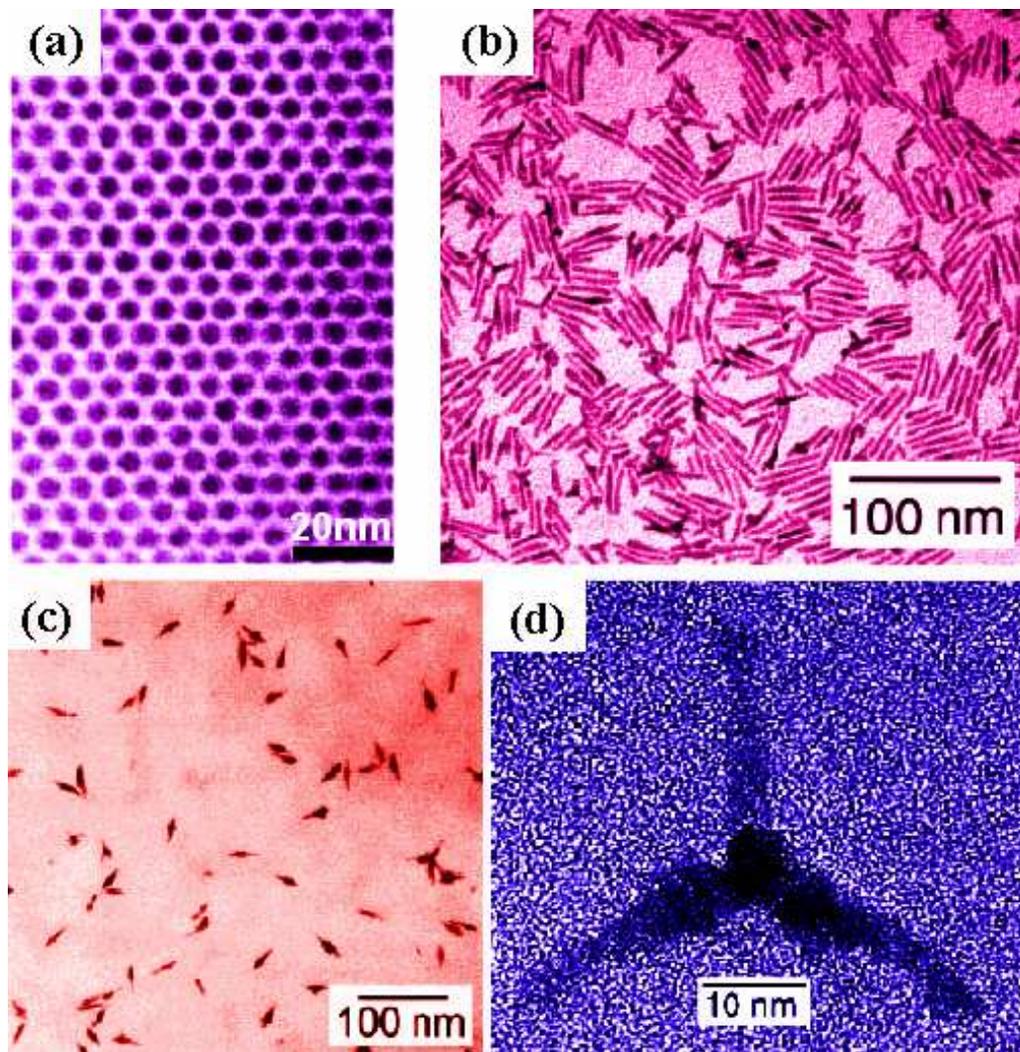


Figure 1.7 Transmission electron microscopy (TEM) images of CdSe nanocrystals of different shapes: (a) Close-packed array of 4.8 nm-diameter nanocrystals. (b) rodlike CdSe nanocrystals with an average length of 34.5 nm and an aspect ratio of 10:1. (c) teardrop shape nanocrystals and (d) tetrapod shaped nanocrystal with its fourth axis pointing out of the plane (reproduced from [91]).

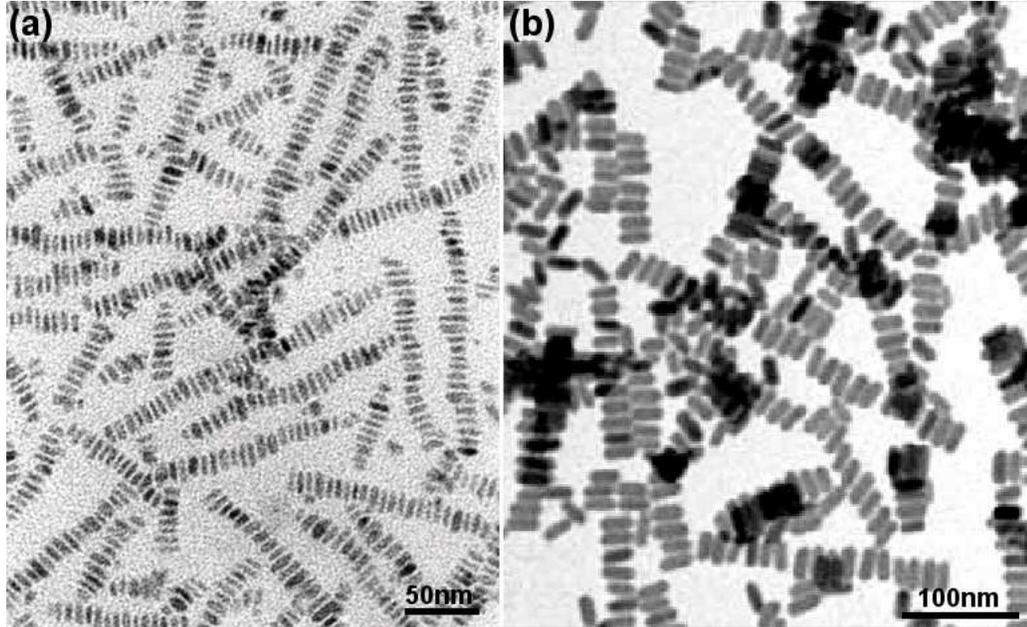


Figure 1.8 TEM images showing ordered chains of surfactant-coated prismatic (a) BaSO_4 and (b) BaCrO_4 NPs prepared in AOT (AOT=bis(2-ethylhexyl)sulfosuccinate) microemulsions at a $\text{Ba}^{2+}:\text{SO}_4^{2-}$ (CrO_4^{2-}) molar ratio of 1:1 (reproduced from [92]).

Compared to nanocrystals, the assembly of NW arrays is more challenging due to the shape anisotropy of the object [18,97]. NW self-assembly generally results in short-to-medium range superlattices with only partial order. It has been reported that single-crystalline NWs of Ag_2Se have been synthesized through a room-temperature template-directing reaction between single-crystalline NWs of trigonal Se (*t*-Se) and aqueous AgNO_3 solutions [98]. In this template-engaged process, the silver ions diffused into the lattices of *t*-Se and formed Ag_2Se without involving significant reorganization of the Se atoms. An interesting diameter-dependent phase transition was also observed in this new NW system: The Ag_2Se NWs were found to crystallise in the tetragonal structure when their diameters were less than ~ 40 nm (Figure 1.9(a-c)). As the lateral dimensions of these NWs increased beyond ~ 40 nm, the orthorhombic structure became the more stable one (Figure 1.9(d)). These uniform Ag_2Se NWs are interesting for their applications as a superionic conductor and thermoelectric material.

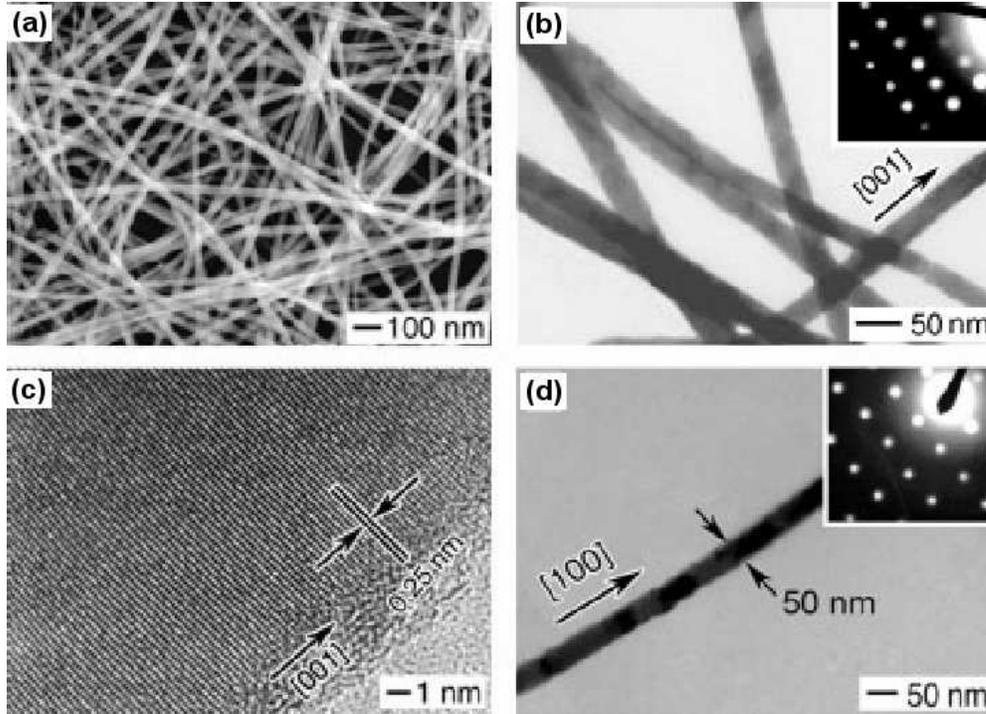


Figure 1.9 (a) An SEM image of α -Ag₂Se NWs obtained by reacting *t*-Se NWs with an aqueous AgNO₃ solution. (b) A TEM image of α -Ag₂Se NWs and the electron diffraction pattern (inset) taken from the middle portion of an individual NW. The diffraction spots can be indexed to the orthorhombic structure. (c) A high-resolution TEM image obtained from the edge of an individual wire, indicating its single crystallinity. The fringe spacing of 0.35 nm corresponds to the interplanar distance of {200} planes, implying that the growth direction of this NW was $\langle 100 \rangle$. (d) A TEM image of an α -Ag₂Se NW ~ 50 nm in diameter. This wire was crystallized in the tetragonal structure, as revealed by its electron diffraction pattern (inset) (reproduced from [98]).

The use of one-dimensional (1D) semiconductor materials as candidate laser materials has attracted significant attention because of the possibility of improved excitonic recombination due to carrier confinement. Chemically grown semiconductor NWs can act as resonators after cleavage of both ends of the NW. Such devices consist of an n-type CdS NW resting on a p-type Si substrate with a metal/alumina film evaporated on top of the NW [99]. Carrier recombination in this

p-n junction resulted in NW electroluminescence. Other nanocrystal and NW optoelectronic phenomena reported include electrogenerated silicon nanocrystal luminescence [100], optically pumped semiconductor NW lasers [101], and electrochromic semiconductor nanocrystals [102].

§ 1.3.5 Directed self-assembled hierarchically structure

When the self-assembly of ordered structures are introduced at different length scales in a single process, hierarchically ordered materials are formed. Hierarchically ordered large crystals and open structures can be constructed through multiple and self-similar growth. The formation of these unusual shapes is related to curvature effects and is independent of the basic structural units [103,104]. Directed self-assembly can provide not only the ability to tune the interaction between individual assembling components but also the ability to position the final assembly at a desired location. For example, electric field assisted self-assembly is used to position nanowires on a pad [105], or to control the orientation of self-assembled patterns in a block copolymer blend [106]. By varying the geometrical constraints on a set of assembling components, different packing orders are obtained. Figure 1.10 shows some examples of the high-order structures, and schematic representations of how they are formed [107]. Figure 1.10(a) shows the primary 5 μm octahedral crystals formed by the $\{111\}$ planes of the cubic phase periodic silicates. A commonly observed rosette-like structure (Figure 1.10(b)) viewed from different angles indicates that these crystals are secondary structures made of primary octahedral subunits shown in Figure 1.10(a). The secondary structure is about 11 μm in width, two times the size of the primary structure, and is based on a quarter-octahedron model with 24 edge-sharing primary subunits. Figure 1.10(c) shows the tertiary octahedral structures containing three subunits on each side. The width of the tertiary structure is 16 μm , roughly three times the size of the primary crystal. Figure 1.10(d) (high magnification) and (e) illustrate even higher order structures about 25 μm in width, which contain five units on each side. Furthermore, a high-order structure consisting of filled tertiary octahedral units is shown in Figure 1.10(f) that still preserves the overall octahedral shape.

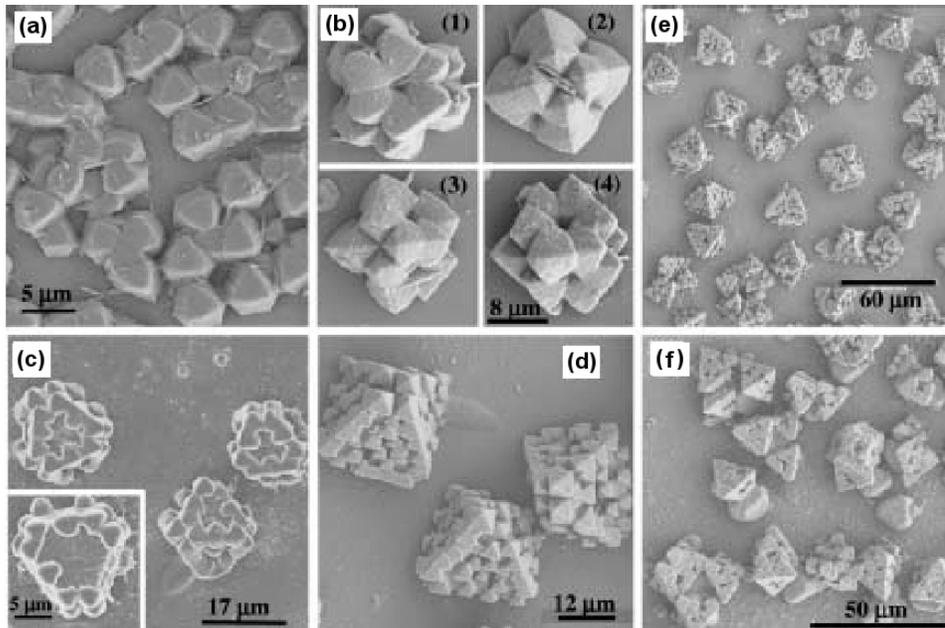


Figure 1. 10 Hierarchically ordered octahedral open crystal silicate structures: (a) Primary octahedral crystals. (b) Secondary octahedral crystals: (1) face-on, (2) top view from one corner, (3) edge-on, (4) tilted edge-on. (c) Tertiary octahedral crystal. (d) Large open octahedral objects containing five primary octahedral units on each side. (e) Large area view of high-order open structures. (f) Large open structures assembled from tertiary units (reproduced from [107]).

Modifying the spatial distribution of the interfacial energy on a substrate can create 2D patterns of oriented nanocrystals. For example, Sounart and co-workers [108] applied microcontact-printing techniques to grow oriented ZnO nanorods (NRs) on patterned substrates. Extended microarrays of carboxyl-terminated alkylthiols were printed on electron-beam-evaporated silver films. When the patterned silver substrates were placed in aqueous zinc nitrate solutions, oriented ZnO NRs formed on the bare silver surfaces, but not on the surfaces covered by the carboxylic acid groups (Figure 1.11(a)). Using this approach, they were able to make patterned lines, dots, and a variety of structures, and control the density and the spacing to micrometre scales (Figure 1.11(b)). Multiple NRs were commonly observed because the NRs were significantly smaller than the patterns (inset in Figure 1.11(d)).

However, single crystal patterning was obtained if the crystals were growing larger than $1\ \mu\text{m}$ (Figure 1.11(b), upper inset). Figure 1.11(c) and (d) present arrays of ordered, flower-like ZnO structures formed by the oriented primary rods. Interestingly, a densely packed array of similar structures is shown in Figure 1.11(e), with which the secondary crystals are almost connected.

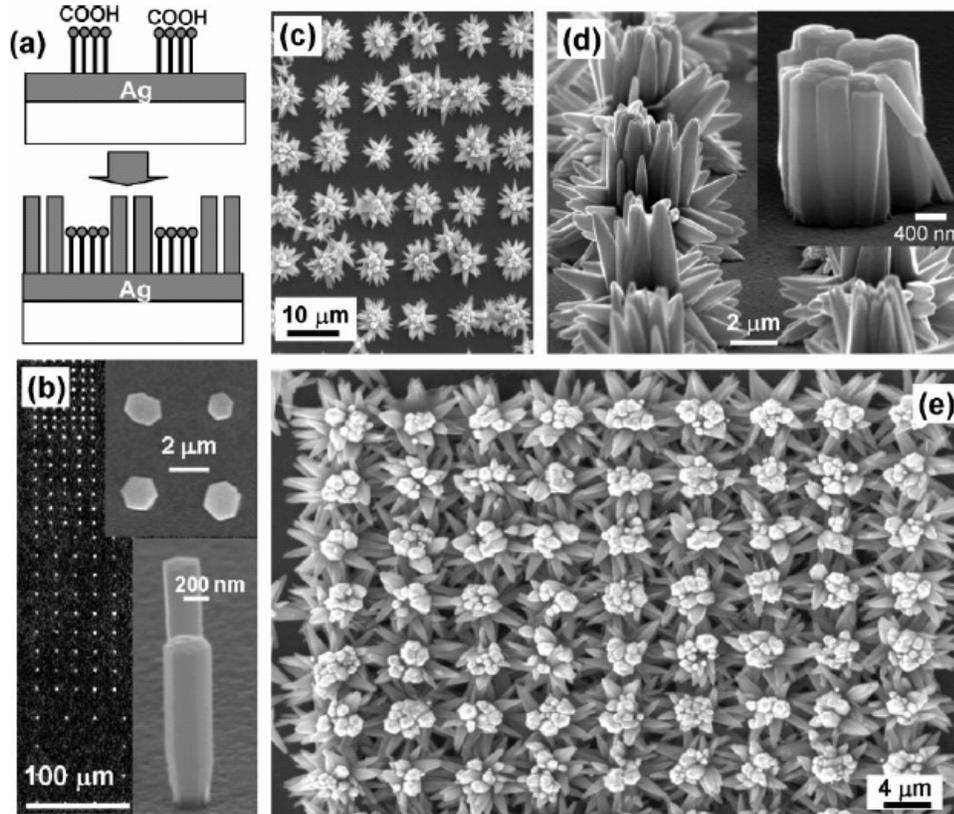


Figure 1.11 Micropatterning of hierarchical ZnO crystals: (a) Schematic illustration of micropattern chemistry for patterned ZnO growth. (b) Dotted patterns of vertically oriented NRs and patterned single crystals (insets). (c) Arrays of separated, secondary flowerlike structures. (d) Side-view of array in (c) with the inset showing the first-generation seed bundles. (e) Dense array of secondary ZnO ‘flowers’. The patterned NR arrays and single crystals in (b) were synthesized on Ag substrates in one growth step after microstamping, and the flowerlike crystals in (c-d) were grown in a second stage on patterned arrays like that shown in (b, lower inset) (reproduced from [109]).

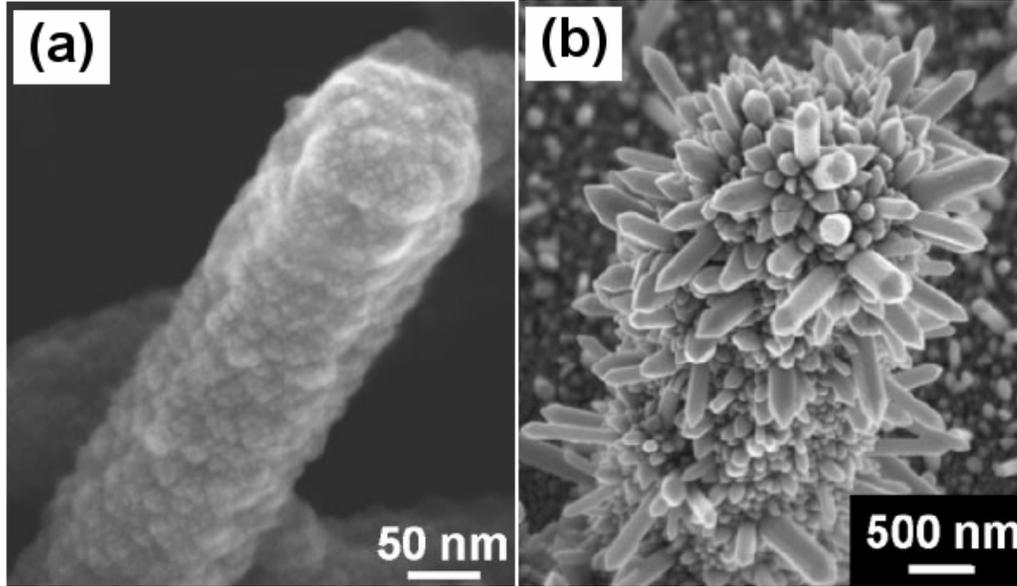


Figure 1.12 (a) ZnO NR coated with CdS NP seeds. (b) CdS NRs on ZnO crystals (reproduced from [Error! Bookmark not defined.]).

Another important extension of the self-assembly of materials is its application in mixed material systems. Recently, Tian and co-workers [107] have also demonstrated stepwise assembly of hierarchical heterostructures by growing cadmium sulfide (CdS) NRs on ZnO crystals. This process involves first nucleating and growing ZnO hexagonal rods (Figure 1.12(a)). In a second step, CdS nanoseeds are nucleated on the ZnO crystal surfaces (Figure 1.12(b)) from a solution containing cadmium nitrate and thioacetamide as a sulfur source. This example of mixed material assembly demonstrates high-quality crystallinity, orientational alignment, and high surface/volume ratios might extend the wider applicability for efficient electron and photo transport in photovoltaics [110] and lasers [111].

§ 1.4 Summary and outline of the thesis

Self-assembly plays a prominent role in making objects, patterns, and functional systems in Nature. Inspired by highly complex, impressive functional

systems demonstrated by Nature, self-assembly has the potential to radically alter how we generate nanoscale components and how we assemble these components into larger systems.

Several approaches for using self-assembly for nanofabrication are already under investigation. They range from molecular manipulation through the use of SAMs and supramolecular chemistry, to much larger systems made by the controlled self-assembly of colloids or directly hierarchical architectures. The products of self-assembly can be used either directly in a device, or indirectly to assist conventional microfabrication processes. In the near future, we anticipate a hybrid approach, combining microfabrication with nanofabrication through self-assembly, to be the dominant method for making devices and systems.

There is no doubt that self-assembly can be utilized to construct a wide diversity of structural types with apparent ease. It is expected that self-assembly will be a cost effective and efficient method for manufacturing nanoscale devices and systems. However, until a functional device is realized in a commercial scenario, self-assembly will still remain an unknown entity as a commercial process.

Therefore, the aim of this work is to establish self-assembly as an efficient synthetic route for the construction of nanometre-scale architectures. We believe that the ability of self-assembly to make precisely assembled structures will fulfill the role as future device elements and produce new chemical and physical phenomena.

In Chapter 2, we review the background information about Liquid-Phase Pulsed Laser Ablation (LP-PLA), which had been used as the major technique to fabricate the nanomaterials in this work. Since LP-PLA had been demonstrated to be an effective and general route to synthesize zero-dimensional NPs or 1D NRs, it is reasonable to expect the LP-PLA approach would have great potential as a means to grow large arrays of hierarchical, complex, oriented and ordered superstructures based on the bottom-up strategy.

Chapter 3 describes the details of the procedure we used to produce the nanomaterials, sample preparation and characterization techniques.

In Chapter 4, we present a successful formation of highly ordered carbon nitride nanostructures by LP-PLA using a graphite and ammonia system. The

exploration of the general mechanisms controlling the nanocrystal ordering was carried out by varying the ablation time, laser fluence, and ammonia concentration. The bonding state, chemical environment, and optical properties of carbon nitride are also described. A better understanding of the processes that govern the self-assembly and ordering of the nanocrystals had been attempted from the atomic level, and a mechanism for the growth pathway is proposed.

In Chapter 5, we develop a two-step strategy to increase the structural complexity based on the Chapter 4 results. The formation and morphological evolution of 2D or 3D carbon nitride hierarchical architectures was extensively studied in this chapter. Via controlling the rate of evaporation, the starting seed solution, the size and the quantity of nanocrystals within the droplet, it was possible to create a range of different morphology nanostructures. It was found that the formation of such complex architectures seems to be an evaporation-driven self-assembly process.

In Chapter 6, we also extend the LP-PLA technique to another material system. We found that a novel hierarchical and self-similar growth process can also happen in ZnO by ablating a zinc plate submerged in aqueous SDS solution.

Finally, Chapter 7 contains the conclusions and discusses possible future work.

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