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Zhong Lin Wang *Editors*

Three-Dimensional Nanoarchitectures

Designing Next-Generation Devices

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Chapter 1
Building 3D Nanostructured Devices by Self-Assembly

Steve Hu, Jeong-Hyun Cho, and David H. Gracias

1.1 The Pressing Need for 3D Patterned Nanofabrication

Macroscale engineering is 3D and most structures around us are machined and assembled with a variety of materials that are precisely shaped and patterned. However, while several methodologies exist for precise patterning and assembly at the nanoscale, they can only be enabled in an inherently 2D manner; moreover, many are serial and extremely expensive processes [1–4]. Top-down methods such as particle replication in nonwetting templates (PRINT) [5] have enabled the mass production of nanoparticles, but they tend to have shapes consistent with only a single layer and limited patterning. Hence, there is a pressing need to develop parallel and cost-effective methods for patterning and assembly of 3D nanostructured devices (Fig. 1.1). In this chapter, we discuss methods that focus on the creation of precisely patterned molecular or engineered building blocks that are then driven to assemble themselves into 3D structures using a variety of driving forces. Some of these methods leverage already existing e-beam and imprint lithographic infrastructure by engineering 3D structures from building blocks that are exquisitely patterned in 2D and then subsequently assembled in 3D. We review the challenges associated with self-assembling methodologies with a focus on lithographically defined building blocks and discuss future challenges and prospects.

It is important to clarify at the outset what is meant by a 3D nanostructured device. We characterize one as being composed of either (a) a homogeneous or heterogeneous material composition or (b) structural elements or patterns with a 1–100 nm size scale resolution. Here, one can draw an analogy to macrostructured functional devices such as cars, houses, or planes. An example of a structure with a homogeneous composition on the macroscale is a bare cement wall, while that with a heterogeneous macroscale composition is a cement wall that is interlaid with a glass window and a wooden door with handles. On the microscale, a composite

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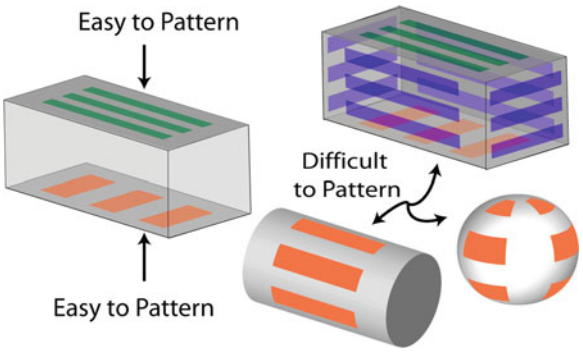

Fig. 1.1 Diagram showing the challenges of fabricating 3D patterned nanostructures. Although it is relatively simple to pattern the *top* and *bottom* of a 3D structure, it is very challenging to pattern perpendicular to the plane or on a curved surface

material such as carbon-fiber reinforced steel has a heterogeneous composition, while glass has a homogeneous composition. This analogy suggests that in general, structures and devices with heterogeneous patterning can provide multifunctionality by leveraging functional traits from each element. Nanoscale engineering seeks to facilitate extreme miniaturization at length scales of 1–100 nm, and there is a need to fabricate 3D structures and devices with both homogeneous and heterogeneous composition and with elements whose sizes range from 1 to 100 nm. One vision for the era of miniaturization was beautifully articulated in Richard Feynman's seminal lecture [6], *There's plenty of room at the bottom*, where he said, "Consider any machine – for example, an automobile – and ask about the problems of making an infinitesimal machine like it." At the present time, human engineering is not even close to creating machines like cars at the nanoscale. In fact, while numerous methods have been developed to grow nanostructures such as spherical or branched nanoparticles, nanorods, nanowires, and nanotubes [7–12], these structures have relatively simple shapes with little or no surface patterning.

Multilayer patterning is essential for the construction of circuits, optical elements, energy harvesting tools, and biomedical devices. Recently, alternative unconventional approaches [13] have been pursued to enable this 3D nanofabrication from the bottom-up. The idea has been put forth that there is a need to build complex structures from precursors using a process that mimics biological assembly. This self-assembly approach focuses on bringing together components with pre-programmed interactions to form organized and functional structures. Self-assembling systems typically consist of components such as atoms, molecules, or larger synthetically structured components. The individual parts can typically interact with each other through a variety of chemical or physical forces. Chemical forces include relatively strong interactions such as those facilitated by covalent and ionic bonds or weak interactions such as hydrogen bonds. Physical forces include interactions driven by electrostatic, magnetic, steric, mechanical stress based, or surface tension forces. These components, when brought together, interact through one of the many forces and self-assemble into organized structures. Typically, components are agitated during self-assembly by a variety of means such as Brownian motion, convection, sonication, or physical shaking. This agitation allows components to

explore different orientations and interactions, ultimately enabling stable structures to form within energy minima. Nature is the master of self-assembly, utilizing this approach to create mostly everything from galaxies to humans to seashells and extending all the way down to microorganisms and nanoscale viruses. On closer examination, molecules are self-assembled aggregates of atoms, proteins are self-assembled aggregates of amino acids, and tissues are self-assembled aggregates of cells. It is well known that natural assembly has two distinct self-assembly flavors, namely equilibrium and non-equilibrium self-assemblies. Self-assemblies at equilibrium do not require energy dissipation to maintain their organization; examples include rocks, mountains, or shells. Such assemblies are typically associated with non-living structures. In contrast, non-equilibrium assemblies need to dissipate energy continuously to maintain their organization; examples include microorganisms, humans, and other animals.

Scientists and engineers have long sought to mimic the naturally occurring self-assembly strategy. There are several examples of functional equilibrium self-assembly structures. The stringing together of monomers such as styrene to form synthetic polymers such as polystyrene is a classic example [14]. Synthetic polymers and supramolecules [15] are essentially the chemist's way of engineering self-assemblies using both strong and weak molecular interactions (i.e., chemical bonds). In Section 1.2, we review strategies to enable aggregative self-assembly of 3D nanostructures using molecular linkages and chemical bonds. In Section 1.3, we review strategies for 3D aggregative self-assembly of nanostructures based on physical forces. Section 1.4 focuses on curving, bending, and folding thin films to form 3D curved and polyhedral nanostructures with the possibility of enabling lithographic patterning in all three dimensions.

1.2 Self-Assembly Using Molecular Linkages

Molecular linkages and chemical bonds can be used to direct self-assembly with remarkable specificity and complexity. Through a hierarchy of molecular interactions, naturally occurring molecules are known to form 3D nanoscale functional structures such as viruses [16]. The remarkable experiment by Fraenkel-Conrat and Williams [17] convincingly demonstrated that infectious (active) tobacco mosaic virus (TMV) particles could be self-assembled (reconstituted) from their protein and nucleic acid components. The TMV is an exquisitely patterned nanostructured helix with a helical radius of approximately 4 nm. Presently, the challenge in the creation of synthetic 3D nanostructures composed of molecules lies in understanding how to design the constituent molecular components that will spontaneously form the final structure. Since the number and types of molecular interactions can be large, the rational synthesis of nanostructures using molecules can be arduous. Nevertheless, there have been several elegant demonstrations utilizing molecular linkages such as ligand–receptors, proteins, and nucleic acids. It is also accepted that as compared to self-assembly with physical forces, chemical linkages can provide selective and complex organization [18].

Apart from all molecular assemblies, self-assembly with molecular linkages is also enabled by surface functionalization which serves to modify the surface properties of inorganic nanoparticles so that they may gain some level of specificity in terms of their interactions. The most general form of molecular interaction utilizes ligand–receptor interactions by attaching a ligand molecule to one particle and its complementary receptor molecule to another [19]. Ligand–receptor-based 2D self-assembly has been used in the past for the construction of self-assembled molecular squares [20]. These squares, which are composed of ligand-assisted attached molecules, can incorporate higher order arrangements of 2D structures like diamonds surrounded by smaller squares. Furthermore, functionalization can improve the durability of self-assembled structures since the ligand–receptor attraction is typically enhanced by a conformational fit.

A secondary improvement in functionalization is the ability for the final assembled product to have inherent sensing or actuation capabilities. Since many of the ligands and receptors are key contributors in well-studied biochemical mechanisms, they are capable of sensing. For example, while hydrogen bonding between base pairs in DNA (which will be covered in a later section) can serve as an impetus for self-assembly, aptamer moieties can interact with proteins present in the environment, thereby providing sensing capabilities. Also, many of these ligand–receptor pairs have specific activation and deactivation conditions like temperature or pH, making it possible for the linkages to be made or broken reversibly [18].

It is self-evident that there are a myriad of ligand–receptor combinations that can be chosen to functionalize inorganic particles. For instance, the use of carbon black [21], β-cyclodextrin [22], and methoxysilanes [23] has all been realized for the self-assembly of 3D nanorods and crystals. In this chapter, we will specifically focus on protein (with emphasis on biotin–avidin/biotin–streptavidin) and nucleic acid applications for functionalization since these are the most domineering areas.

1.2.1 Three-Dimensional Self-Assembly Using Protein Linkages

Proteins are ideal for assembling complex nanostructures for many reasons. First, each protein displays a unique conformation in order to ensure specificity, guaranteeing that it will bind strongest when the arrangement and composition of its substrate are correct. Second, proteins can have multiple recognition sites or binding domains, which grants these molecules with an inherent 3D ligand-binding capability. Finally, proteins are easily modified; their structures can be genetically edited [24] to omit or add certain binding subunits.

Several 3D nanostructures composed solely of protein constituents have been demonstrated. The shapes range from nanofibers [25] to nanotubes [26] to protein cages [27] and can be designed at a high level of specificity. Typically, the required proteins are chosen from the Protein Data Bank, which stores the structural information of many characterized proteins. This choice allows for the selection of structural or binding motifs like a terminal α-helix thereby enabling greater control

over binding sites. After the systematic selection of these proteins, it is also possible to modify their binding characteristics by varying conditions such as pH [25] or engineering specific regions [28].

Since proteins assemble with high specificity, they can be used in conjunction with nanoparticles through surface functionalization. Functionalization of inorganic particles using proteins can be done using multiple strategies. For example, nanoparticles composed of noble metals such as gold can be first thiolated and subsequently cross-linked with a desired protein's amine group through the use of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide/*N*-hydroxysuccinimide (EDC/NHS) reaction scheme [29]. Other charged inorganic nanoparticles like silica can be functionalized by using proteins with charged amino acid residues like lysine, a method which has been applied to form shapes like hollow spheres [30].

One very popular method of functionalizing inorganic molecules is achieved by using the proteins avidin or streptavidin in conjunction with the ligand biotin, a coenzyme. Both avidin and streptavidin are tetrameric proteins which contain four identical binding sites to biotin. The binding strength of biotin to its protein receptor site is extremely strong; it is comparable to that of a covalent bond with a binding constant, K_a, of 1×10^{15} M [31]. With such a high binding strength, the biotin–avidin pair works well in self-assembly, since covalently linked structures are quite stable. Having multiple sites for a ligand can also introduce hierarchical capabilities, where a primary scaffolding molecule can serve to "host" a number of surrounding molecules during assembly.

Let us examine a biotin–streptavidin linkage that has proven successful in 3D self-assembly of inorganic nanostructures. Ferritin is a protein–metal conjugate that is made of a protein shell which encapsulates a ferric oxide core. For biotinylation, ferritin can use its external lysine residues to bind up to 60–70 biotin molecules by a nucleophilic reaction [32]. Once the ferritin has been biotinylated, streptavidin can be added at varying ratios in order to provide adequate streptavidin for cross-linking. However, the streptavidin concentration cannot be too high or it may prevent biotinylated particles from linking to the same streptavidin protein. In one study, this optimal ratio was measured to be approximately one biotinylated ferritin to six streptavidin [32]. To build a 3D nanostructure, biotinylated ferritin can be linked to a primary structure such as a carbon nanotube [33] through hydrophobic interactions to enable the self-assembly of a multilayer nanotube composed of different material layers. An additional concentric layer of a different inorganic metal could also be linked onto this ferritin shell by adding other biotinylated metals.

Another example of controlled self-assembly using biotin–streptavidin can be exemplified through the end-to-end binding of gold nanorods in an experiment performed by Caswell et al. [34]. Biotinylation in this case was achieved using biotin disulfides, which can form disulfide linkages to gold surfaces. Since the nanorods were controllably formed using a cetyltrimethylammonium bromide (CTAB) surfactant, functionalization was hypothesized to only form at the ends of the rods where CTAB was not present. Therefore, the addition of streptavidin would only self-assemble the nanorods end to end instead of connecting them at the sides (Fig. 1.2).

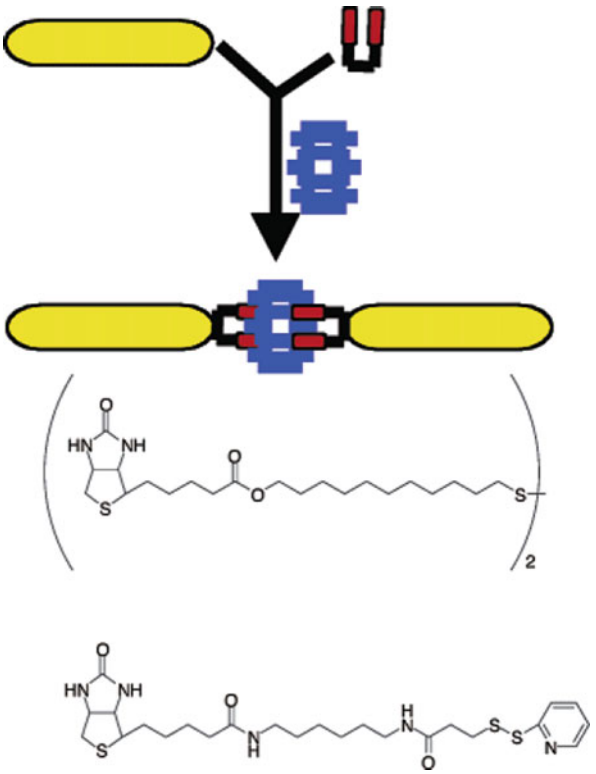

Fig. 1.2 Scheme showing the assembly of gold nanorods (*golden ovals*) by surface functionalization with the biotin disulfide (*red*), and subsequent addition of streptavidin (*blue*) to produce aggregates of nanorods. The chemical structures of the two biotin disulfides are also shown, homemade (*top*) and commercial EZ-Link Biotin-HPDP (*bottom*). Reprinted with permission from [34]. Copyright 2003 American Chemical Society

With the many available methods to biotinylate different inorganic particles, it is possible to create complicated self-assembled structures. In addition, direct control over the region which is biotinylated and the concentration of streptavidin or avidin grants control over the complexity of the assembled structure. Therefore, by using this simple ligand–protein construct, we can expand the possibilities in constructing devices with differing shapes and metal compositions.

1.2.2 Three-Dimensional Self-Assembly with DNA Linkages

Another exciting field enabling the creation of 3D nanostructures is DNA self-assembly. Just like proteins have many benefits for their use in self-assembly, DNA also has significant advantages for its use. DNA is extremely well understood in terms of base pairing and crystallographic structure, making it very predictable and programmable when used as a template for self-assembly [35]. From basic biology, we know that adenine will preferentially bind to thymine, and cytosine will preferentially bind to guanine by hydrogen bonding. Therefore, the assembly of DNA is already quite intuitive from a scientific standpoint.

DNA self-assembly is utilized in two categories for 3D self-assembly: the use of DNA motifs to create origami-like structures made of pure DNA [36] and the use of DNA as a nanoparticle scaffold by functionalization for assembly [37]. The latter portion of DNA technology is very similar to that of protein self-assembly, where the binding originates from specific linkers. Both schemes have brought much potential to enable the creation of devices that can be applied as biosensors, nanophotonic devices, nanoelectric devices [38], and drug delivery vehicles [39].

The folding of 3D DNA structures began with the work of Nadrian Seeman. In 1991, Seeman was able to synthesize a cube solely made from ligated DNA strands by using sticky ends as a linking device [40]. Each vertex of the cube had to be meticulously connected in order to form the final structure, making it a very difficult, low-yield task. Instead, researchers explored other options by starting from stable DNA structures to make 3D nanostructures.

One simple structure is a DNA junction, which is a point where multiple strands of DNA meet via a complementary linkage or through the use of a tris-linker [41]. The junctions allow one to form a DNA folding template, where the structure is already connected and only requires binding intramolecular regions to gain 3D architecture. In one method, a 1669 nt single strand of DNA with multiple junctions was designed with complementary terminal branches. With the assistance of smaller linker sequences, the strand could form crossovers in the center which brought the terminal branches together to form a 3D octahedron [42].

The discovery of the rigidity of triangular-based DNA structures lent credence to the notion that DNA motifs could be used for complicated 3D assembly. The triangular-based structures include trisoligonucleotides (three strands joined by a center tris-linker) and tetrahedrons. The trisoligonucleotides were shown to be able to produce a dodecahedron by utilizing complementary strand sequences as connectors and the center as a vertex [41]. Tetrahedrons are especially viable due to their simple construction protocol; it has been demonstrated that four equal oligonucleotides with complementary regions for each other could be annealed and ligated to self-assemble a DNA tetrahedron with high yield [43]. The tetrahedrons can then be used for advanced functions like protein encapsulation [44] and structural (i.e., bending, twisting) modifications by activating hairpin sequences [39]. In addition, by using a DNA linking strand, it is possible to add a higher level of complexity by assembling multiple tetrahedral DNA motifs [43].

One DNA self-assembly experiment involved the use of DNA "tiles," which are star motifs that can contain multiple symmetric points. A three-point star tile contains a long central strand, three medium strands, three short exterior strands, and three central loops [45]. Each point's end contains a sticky end to be able to latch onto the points of other identical tiles. It was discovered that the length of the central loops allowed for control over the self-assembly of the tiles. Lengthening the loop meant the tile had more curving flexibility and could form 3D shapes more readily through exposing the sticky ends. This, in conjunction with a relatively low DNA tile concentration to increase the chance of connected structures to interact, allowed for the self-assembly of tetrahedral-shaped structures (Fig. 1.3). By adding more DNA tiles and shortening the loop to reduce strand bending, dodecahedrons

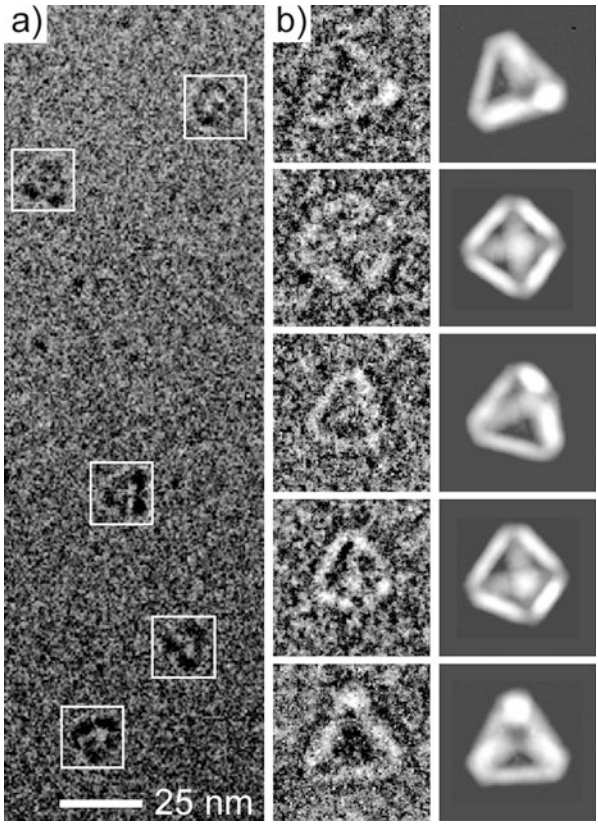

Fig. 1.3 Characterization of the DNA tetrahedron by DLS, AFM, and cryo-EM. (**a**) A representative cryo-EM image. *White boxes* indicate the DNA particles. (**b**) Raw cryo-EM images of individual particles and the corresponding projections of the DNA tetrahedron 3D structure reconstructed from the cryo-EM images. These particles are selected from different image frames to represent views at different orientations. Reprinted with permission from [45]. Copyright 2008 Macmillan Publishers Ltd (Nature Publishing Group)

and buckyballs [45] were formed, possibly arising due to the smaller curvatures of these larger 3D structures. The same phenomenon is observed in five-point stars as well, where longer loops and lower DNA concentrations are found to produce icosahedrons [46].

To simplify DNA folding, a later technique called DNA origami [47] was developed by Paul Rothemund, which involved the use of a long strand of DNA as a large scaffold with hundreds of specific "staple" DNA strands to form crossovers which tighten or bend the scaffold. These staple strands are meticulously programmed to form desired crossovers at repeated turn length intervals through the use of a DNA software system that can pattern the complementary sequences. By using this technology, one can form DNA templates for folding 3D nanostructures with great precision. One experiment displayed the folding of a nanoscale DNA box with a

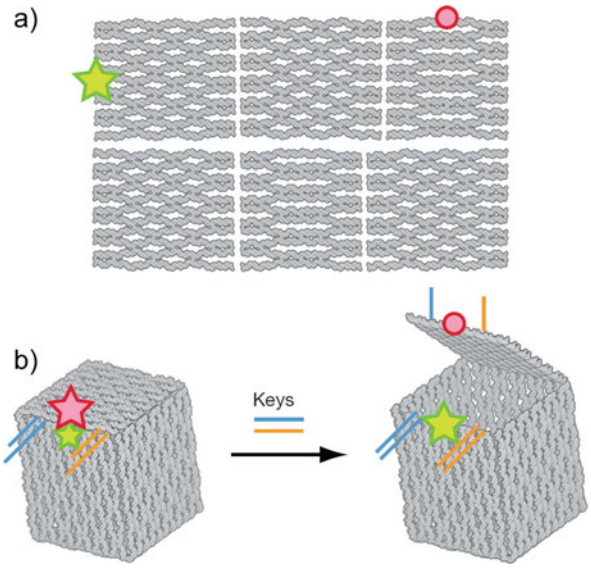

Fig. 1.4 Programmed opening of the box lid. Illustrations of the unlinked faces of the box (**a**) and the controlled opening of the box lid (**b**). The emission from the Cy5 and Cy3 fluorophores is marked with *red* and *green stars*, respectively. Loss of emission from Cy5 is denoted by a *red circle* and the independent lock–key systems are indicated in *blue* and *orange*. Reprinted with permission from [48]. Copyright 2009 Macmillan Publishers Ltd (Nature Publishing Group)

controllable lid [48] through the use of DNA origami by starting with a linked template of six DNA squares. The staple strands assisted in the folding of the squares to form a cubic structure with specific sticky ends to grant complementary oligonucleotide "keys" access to open the box with a conformational change (Fig. 1.4).

DNA, like biotin–streptavidin, can also be used for the self-assembly of inorganic particles through functionalization. There are multiple methods used to tether a strand of DNA to an inorganic nanoparticle. Some involve using charge interactions [49] since DNA is negatively charged, while some metals have cationic properties. These interactions can allow DNA to become a template on which metal nanoparticles may aggregate [50]. Another common functionalizing technique uses gold–thiol linkages to the thiolate DNA [38, 51, 52]. Like the arrangement of protein-linked nanoparticles, DNA-functionalized nanoparticles have high specificity since they will only bind to complementary strands.

Binding specificity was demonstrated through an experiment involving different sized gold particles (diameters of 8 and 31 nm) that were functionalized with complementary oligonucleotides [53]. The particles self-assembled to form a "satellite" structure, which is distinguished by a large central particle surrounded by multiple linked smaller particles (Fig. 1.5). When the oligonucleotides were omitted from these particles, self-assembly did not yield any organized structure [53]. This self-assembly has been applied to not only nanoparticles but also nanostructures like gold nanorods [54]. Added complexity is also possible through the use of biotinylated oligonucleotides that are functionalized onto nanoparticles [55]; streptavidin can be added after hybridization to induce stepwise assembly.

DNA self-assembly is one of the best understood molecular technique today simply because of our ability to manipulate DNA easily. The biological and materials

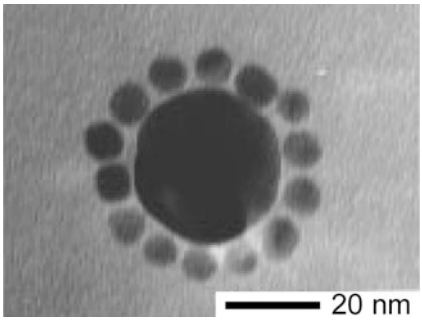

Fig. 1.5 TEM image of the binary nanoparticle network materials supported on holey carbon grids. A nanoparticle satellite structure obtained from the reaction involving 120:1 modified 8 nm particles:modified 31 nm particles and linking oligonucleotides. Reprinted with permission from [53]. Copyright 1998 American Chemical Society

device applications are not trivial, and additional functions can be made with ease. There has been some work to date on RNA self-assembly involving magnesium-mediated RNA and its receptor loop RNA to produce self-assembled gold nanowires [56]. Functionalization occurs through the use of DNA–RNA complementary binding regions secondary to a primary DNA thiol linkage to gold.

1.3 Three-Dimensional Self-Assembly Using Physical Forces

While self-assembly with molecular linkages provides remarkable versatility and specificity in terms of the kinds of interactions that can be engineered, many of these linkages fall apart when the structures are dehydrated or heated. Hence, there is a need to explore the assembly of structures using physical forces. Moreover, devices with magnetic, photonic, or electrical properties often require the incorporation of inorganic components such as metallic or semiconducting materials [57]. There is often a need to organize metallic and inorganic components with nanoscale precision to enable functional 3D nanostructured devices. In this sense, it is already established that self-assembly provides an attractive route to fabricate nanoscale structures [58].

Three-dimensional methods build upon conventional 2D self-assembly methods. The 2D methods typically form arrays or monolayers of nanostructures. Most of these 2D structures are formed by utilizing a physical force to coax nanoparticles into their desired places. For example, the use of surface interactions in Langmuir–Blodgett films at the air–liquid interface can be applied to generate the self-assembly of a monolayer of nanoscale particles [59] and even nanorods [60]. Other methods have involved evaporating thin liquid films over a solid support [61–63]. The 2D self-assembly of an array or monolayer of nanoscale particles by evaporation is driven by capillary forces that pull particles together during removal of the liquid.

After evaporation, the particles are held together by van der Waals or dispersion forces.

To move into the third dimension, one approach focuses on shape control, namely, by synthesizing colloids with a 3D morphology. These inorganic particles are fabricated in solvents with varying pH, concentration, temperature, and voltage; the resulting nanostructures have complex 3D morphologies and resemble flowers, helices, discs, and hollow boxes [64–66]. Another example involves the self-assembly of CdSe quantum dot superlattices by a nucleation-caused crystallization in solution; the lattices are then held together by intermolecular forces [67]. Dipole–dipole interactions are also utilized to create 3D rod-like structures with anisotropic control using a surfactant [68].

The use of physical templates to shape the overall self-assembly has enabled control over both the arrangement and the interactions among constituent particles. Templates can also be structured using electron beam lithography, imprint lithography, particle track etching, or by anodization. Self-assembly of a hexagonal closed packed or face-centered cubic silica colloidal crystal has been demonstrated using a uniform template; small defects in the template reflect small defects in the crystal [69]. By constricting the volume of the template on the nanoscale, one can produce a wide range of structures [70] (Fig. 1.6). Linked templates are also used, which involve a chemically functionalized template to bind to a specific inorganic compound. This helps to produce a hierarchical self-assembly [71], where inorganic molecules can link onto an initial self-assembled structure and then build upon it to form complicated structures such as sieves [72]. The linked template method has been mastered to the extent to which even a nanoscale painting by Picasso [73] has been replicated using colloidal gold!

Van der Waals or dispersion forces are widely used to hold together nanostructured organizations after self-assembly. However, it should be noted that this force is weak, and the nanostructures can often be disrupted by sonication. For example, the cubic assemblies shown in Fig. 1.7 were formed by self-assembly of selectively functionalized hydrophobic units in water. Here, selective functionalization of different faces of silver (Ag) cubes was achieved using hydrophobic (octadecanethiol) and hydrophilic (mercaptohexadecanoic acid) thiols. Selective functionalization results in the formation of linear chains and closed packed crystals; however, the units are held together only by weak van der Waals forces [74]. Similar assemblies were demonstrated using nanowires with amphiphilic segments [75] and were even observed during dissolution of the templates (Fig. 1.8a) [76]. These 3D nanostructures, although self-assembled in impressive 3D geometries, would fall apart upon sonication. Self-assembly with segmented nanowires provides some specificity in the interactions by the inclusion of hydrophobic, hydrophilic [75], or magnetic (Fig. 1.8c–d) segments [77].

Permanent bonding of units after assembly can be achieved using surface tension-based assembly with liquid drops that solidify on cooling or cross-linking. This approach draws inspiration from mesoscale self-assembly approaches [78–81] to permanently bond nanoscale assemblies using adhesives [82] (Fig. 1.8e–f) or solder [83]. These bonded assemblies survive sonication. Additionally, selective patterning

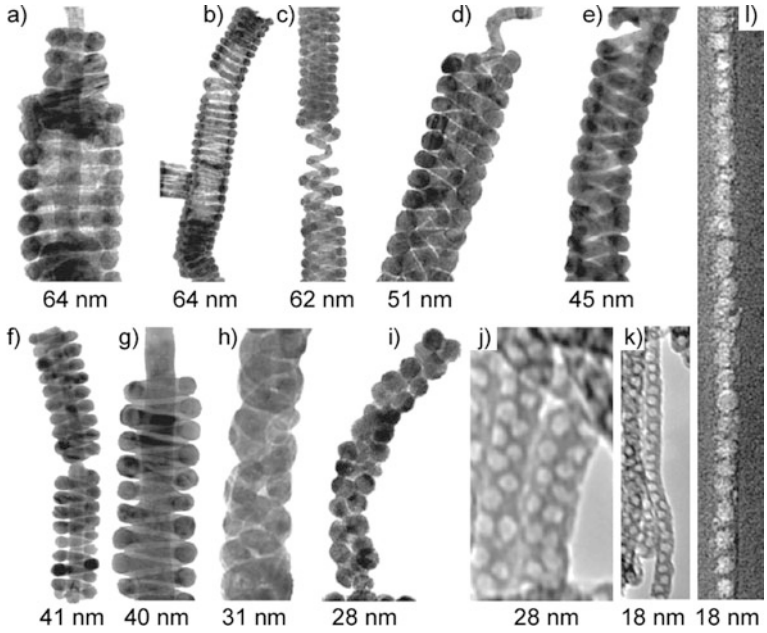

Fig. 1.6 Representative TEM images of mesostructures formed inside alumina nanochannels with differing confinement dimensions. The confining nanochannel diameter is indicated underneath each image. (**a–i**) Silver inverted mesostructures prepared by backfilling the confined mesoporous silica; (**j–k**) free-standing mesoporous silica fibers; (**i**) mesoporous silica embedded inside the alumina nanochannels obtained using a focused ion beam for sample preparation. The structures are (**a**) three-layer stacked *doughnuts*; (**b**) S-helix; (**c**) core–shell D-helix, in which the core and the shell are both S-helix; (**d**) core–shell triple helix, in which the shell is a D-helix and the core is an S-helix; (**e**) D-helix; (**f, g**) S-helix with a straight core channel; (**h**) D-helix; (**i, j**) inverted *peapod* structure with two lines of spherical cages packed along the long axis of the alumina nanochannel; (**k, l**) inverted *peapod* with one line of cages. Reprinted with permission from [70]. Copyright 2007 Macmillan Publishers Ltd (Nature Publishing Group)

of segments of nanowires with self-assembled monolayers enables specific bonding of these segments with hydrophobic monomers that can be subsequently cross-linked (Fig. 1.8f).

1.4 Three-Dimensional Patterned Nanofabrication by Curving and Bending Nanostructures

One attractive strategy to enable patterning in 3D is to leverage precise 2D nanofabrication paradigms to create units that are then rotated or bent into the third dimension. The forces required to achieve this curving or bending can be derived from several mechanisms including thin film stresses, magnetism, pneumatics, swelling, and surface tension [84]. Most of the prior research involving the above mechanisms has been limited to the microscale. Here, we focus on two mechanisms