

Three dimensional self-assembly at the nanoscale

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ABSTRACT

At the nanoscale, three dimensional manipulation and assembly becomes extremely challenging and also cost prohibitive. Self-assembly provides an attractive and possibly the only highly parallel methodology to structure truly three dimensional patterned materials and devices at this size scale for applications in electronics, optics, robotics and medicine. This is a concise review along with a perspective of an important and exciting field in nanotechnology and is related to a Nanoengineering Pioneer Award that I received at this SPIE symposium for my contributions to the 3D self-assembly of nanostructures. I detail a historical account of 3D self-assembly and outline important developments in this area which is put into context with the larger research areas of 3D nanofabrication, assembly and nanomanufacturing. A focus in this review is on our work as it relates to the self-assembly with lithographically patterned units; this approach provides a means for heterogeneous integration of periodic, curved and angled nanostructures with precisely defined three dimensional patterns.

Keywords:

Nanofabrication, nanotechnology, polyhedra, lithography, metamaterials, nanomanufacturing, origami, self-folding

1. INTRODUCTION AND BACKGROUND

The fabrication of three dimensional structures and devices is commonplace on the macroscale but becomes increasingly difficult at small size scales. This challenge is rooted in the fact that conventional top-down fabrication at micro and nanoscale was developed primarily for integrated circuit fabrication [1]. This fabrication approach is based on the transfer of a CAD pattern onto a planar mask and then onto a planar substrate, and is thus inherently a two dimensional pattern transfer process. A number of methods have been developed to fabricate and pattern three dimensional micro and nanoscale objects using top-down methods including wafer bonding [2], stereolithography [3], printing [4], focused ion beam methods [5], anisotropic etching [6], molding and related techniques [1, 7-10]. However, there still exist significant challenges in 3D fabrication most notably in the parallel fabrication of precisely patterned nanostructures with periodic, curved and angled geometries.

Self-assembly is a biologically inspired bottom-up approach to form ordered structures from constituent units via pre-programmed interactions between them. It is well known that atoms can interact with each other to form assemblies ranging from small molecules to large periodic crystals through covalent, ionic or metallic bonds. In contrast to such bonding, the word self-assembly originally was used to describe the organization of molecules using weak interactions such as van der Waals, hydrogen bonding or distributed weak electrostatic interactions such as interactions between ions and induced dipoles. Early use of the word *self-assembly* can be traced as far back as the 1960's when scientists realized

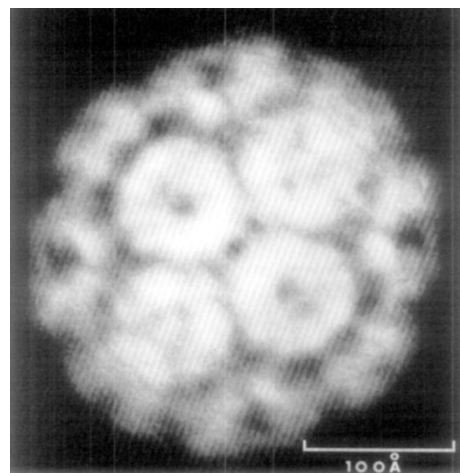


Figure 1 An example of a self-assembled 3D biological nanostructure. Electron micrograph average image of the cowpea chlorotic mottle virus (CCMV) which infects the cowpea plant. Image reprinted from reference 11 with permission from Elsevier; © 1967 Elsevier. This nanostructure with icosahedral symmetry self-assembles from constituent protein and RNA molecules.

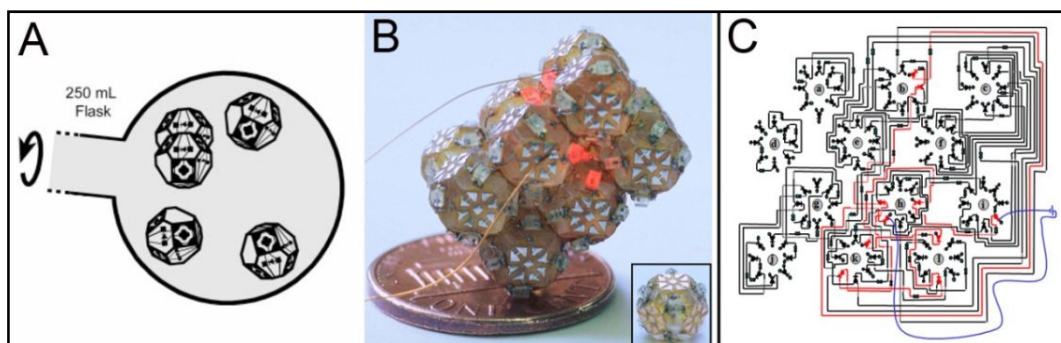


Figure 2 An example of mesoscale 3D self-assembly with millimeter scaled units. Self-assembly of millimeter scaled 3D electrical networks with serial connectivity. Reprinted from reference 35 with permission from AAAS; © 2000 AAAS.

that they could reconstitute naturally existing three dimensional biological structures such as viruses from their constituent biomolecules [11]. Chemists and biochemists have made significant in the area of three dimensional molecular self-assemblies ranging from early advances in biomolecular assembly [12], molecular complexes [13], host-guest chemistry [14], supramolecules [15], vesicles [16] and reconstituted viruses [11, 17] (**Figure 1**) to more recent research on foldamers [18], metal organic frameworks [19], complex inorganic structures [20], DNA nanostructures [21, 22], block copolymers [23], peptide nanofibers [24], vesicles and liposomes [25], and synthetic molecular motors [26]. Since they can feature a range of hierarchical interactions, molecules can be thought of as the most diverse and exquisite set of building blocks for self-assembly. However, molecular assemblies often fall apart in non-aqueous media or degrade on heating, thereby limiting their applicability. Further, it can be challenging to incorporate the types of modules

such as high-performance resonators or transistors that would be required in optical or electronic circuitry. It is noteworthy that to address this challenge, a major recent focus in the area of self-assembly with biomolecules has been to utilize biomolecules to direct the assembly of inorganic nanoparticles such as colloids, nanowires and quantum dots [27-29], but integration, function and performance still remains a significant challenge.

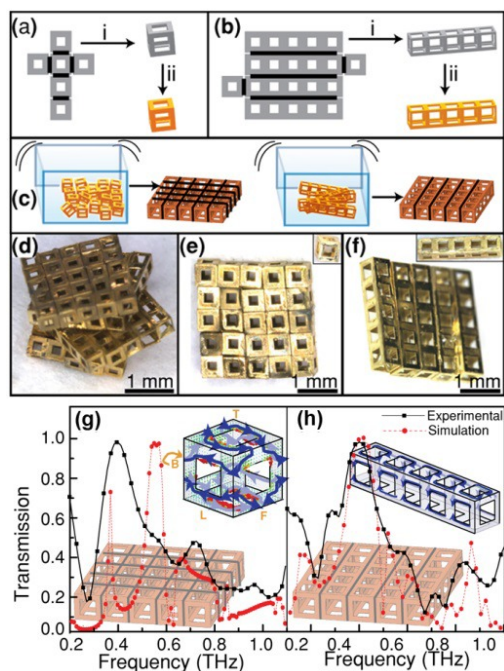


Figure 3 An example of 100 micron scale self-assembly of polyhedral electromagnetic metamaterials. These metamaterials enable current loops to flow in all three dimensions on excitation with electromagnetic radiation resulting in pronounced peaks in the transmission spectrum. Reprinted from reference 64; © 2010, American Institute of Physics.

Beginning in the 1990's, researchers began to adapt the methodology of self-assembly for use with non-molecular and non-spherical mesoscale units directed at applications in robotics, optics and electronics [30-40]. Mesoscale self-assembly referred to the self-assembly of millimeter and centimeter sized units. Following in the tradition of earlier work in the late 1950s on self-replication with mechanical pieces [41], these mesoscale units could be readily fabricated by hand and easily visualized by the naked eye thereby facilitating the interrogation of model systems to investigate the influence of a variety of parameters on self-assembly. Research in mesoscale assembly convincingly demonstrated that smart units can self-assemble on their own into complex structures based on a variety of mechanisms including shape recognition [42], steric constraints [43], hierarchy of forces [44] and patterns of binding sites [35, 45]. In fact, very complex assemblies could be formed with the appropriately designed units. For example, it was shown using 5 millimeter scaled truncated octahedra shaped units patterned with devices (light emitting diodes), wires, and arrays of low melting point solder bumps, that 3D electrical networks could be formed merely on tumbling the units in a density matched liquid that was heated above the melting point of the solder bumps [35] (**Figure 2**). Here, what was remarkable was not just that the units aggregated but rather that solder bump-on-bump connections were formed during assembly, in a well-defined manner. Such connections caused the LEDs to connect with each other in

either serial or parallel networks that form the basis of all connections in electronic devices.

Going down in size from the mesoscale, self-assembly with microscale units has also been used effectively to create a variety of three dimensional structures including optomechanical devices [46], curved displays [47], solar cells [48], microfluidic networks [49], untethered surgical tools [50, 51], polymer microcapsules [52-55], tissue scaffolds [56, 57], patterned particles [58-60], and crystals and arrays composed of spherical [61, 62] and polyhedral units [63, 64]. One example highlighted in **Figure 3** illustrates the hierarchical self-assembly of polyhedral metamaterials using two independent self-assembly steps [64]. First, surface tension based solder self-assembly was used to fold up cubes and parallelepipeds. The polyhedra were then functionalized with a hydrophobic self-assembled monolayer and a hydrophobic adhesive was precipitated on their surfaces causing them to aggregate in water. After self-assembly, the adhesive could be cured by UV initiated polymerization to form permanently bonded polyhedral metamaterials. In these materials, metallic polyhedra are insulated from their neighbors via the polymeric adhesive coating on their surfaces. Hence, the self-assembly approach provides a means to pattern microscale metallic lines in 3D within a dielectric background. Since the polyhedra have features in the 100 micron range, they elicit pronounced responses in the THz region of the electromagnetic spectrum. Importantly, as compared to stacked metamaterials [65], such polyhedral metamaterials allow induced current loops to flow in all three dimensions as can be seen in the inset in **Figure 3**. The interaction of these current loops result in well pronounced spectral peaks and this approach may also enable the creation of truly isotropic metamaterials.

In terms of design, at a minimum, interesting self-assembly systems must possess three ingredients. These are (a) units, (b) interactions, and (c) agitation. The accomplishments of mesoscale self-assembly were made possible by the ability to readily create a variety of patterned units, often made by hand, while those in molecular assembly are enabled by the ability to create diverse molecules using synthetic organic chemistry or rational peptide or oligonucleotide synthesis. Interactions between units can be engineered using a variety of chemical and physical means such as hydrogen bonding, van der Waals, capillary, magnetic, electrostatic and steric forces. In mesoscale assembly, agitation was introduced via tumbling, bubbling gases, or shaking while on the sub-micron scale, agitation is naturally present in thermal energy commonly recognized as Brownian motion. Fine tuning of the assembly is achieved by manipulating the relative strength of the agitation with respect to the various local energy minima; this tuning is an important factor in designing assemblies with few defects. Ideally, one needs to engineer potential energy surfaces that feature few local energy minima while at the same time featuring deep, sharp-edged, funnel-shaped global energy minima. For example, as shown in **Figure 4**, when we self-assembled cubes by the principle of minimization of surface area of hydrophobic regions (indicated by the yellow color) in water, we observed that not all patterns work equally well. In fact, we studied and modeled this interaction and observed that geometric patterns with large overall areas, high angular distributions and low radii of gyration minimized defects [66]. Essentially, as seen in **Figure 4**, pattern II results in interactions that feature sharp localized energy minima as compared to interactions of units with pattern I which can get easily trapped in broad local energy minima. These trapped states are not easily disrupted by agitation and result in defective assemblies. The defects can be seen in the assembly shown in the inset where units with pattern I are shifted relative to each other. A general theory of designing energy landscapes between solid or deformable units interacting via a variety of forces is essential to effective self-assembly, but is lacking.

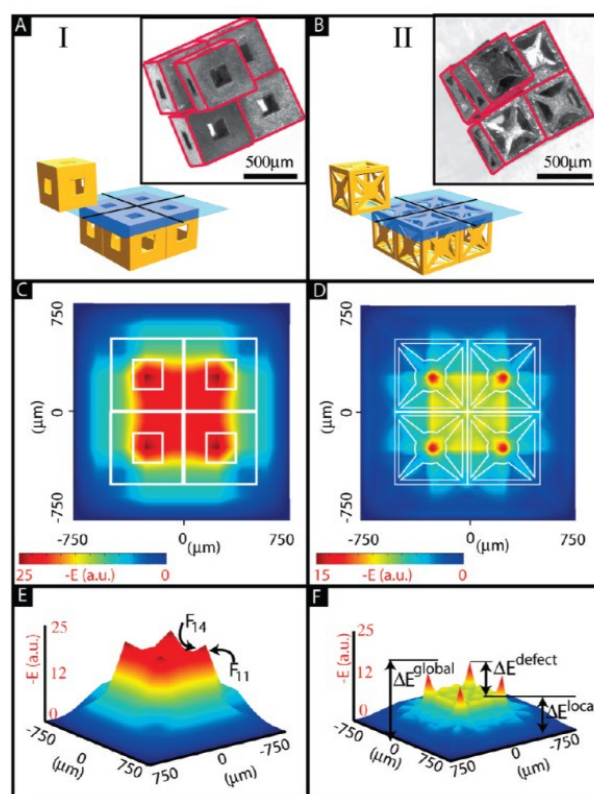


Figure 4 Tuning inter-unit interactions in the self-assembly of cubes via surface patterns. Schematic, experimental images, and equilibrium energy diagrams of the interactions of hydrophobic cubes with two different patterns, I and II. Reprinted from reference 66; © 2010, American Chemical Society.

This article is focused on the self-assembly of 3D structures with dimensions ranging from 1 to 100 nm using non-molecular building blocks and specifically directed towards self-assembly with lithographically patterned units. Three dimensional nanoscale self-assembly using non-molecular building blocks is especially challenging for a variety of reasons. Firstly, 3D top-down nanoscale patterning is extremely difficult and often cost-prohibitive so it is hard to design precisely patterned units and building blocks for self-assembly. The bottom-up growth and spontaneous patterning of nanostructures has made great strides [67-71], but it is still not possible to create precisely patterned 3D nanostructures. I first describe our results on combining the top-down method of electron beam patterning with the bottom-up method of self-assembly via folding to create precisely patterned curved and polyhedral nanostructures. I also discuss strategies that can be utilized to form aggregates of nanostructures that are well bonded and form electrical connections during assembly.

3. RESULTS AND DISCUSSION

Self-assembly of curved nanostructures

Patterning strain in thin films can cause them to curve and bend spontaneously, so in principle one can use these forces to self-assemble curved nanostructures [72]. An early example was elegantly demonstrated using molecular beam epitaxially grown InAs/GaAs bilayer films which spontaneously self-assembled by rolling into tubes with inner diameters as small as 2 nm on etching an underlying sacrificial AlAs layer [73]. Indeed, since the pioneering work of clockmaker John Harrison in the 18th century, it is well known that well adherent bilayers will spontaneously bend due to differences in thermal expansion coefficients [74]. So in principle, one can extend his concept and utilize differential stress in bilayers to fabricate 3D curved structures. However, on substituting values for the thermal expansion coefficients of common metals in well-established bilayer mechanics models, such as the one derived by Timoshenko [75], one quickly realizes that one can only achieve differential strains of a fraction of a percentage using thermal expansion even with temperature differences on the order of a hundred degrees. This small magnitude of differential strain is only sufficient to curve even very thin (on the order of 1 nm) films with microscale radii but not nanoscale radii since the radii of curvature are in the range of 200 x (film thickness). Hence, an important challenge is to understand how to utilize deposition and related processing conditions to generate large strains in thin films. One such example is the previously mentioned heteroepitaxial deposition of bilayers generating radii of curvature in the range of approximately 7 x (film thickness). However, molecular beam epitaxy (MBE) is an expensive and not easily accessible process since MBE requires ultra-high vacuum, is a slow process and also typically developed for compound semiconductors. Nevertheless, strain engineering with MBE films has been widely utilized to create a variety of 3D self-

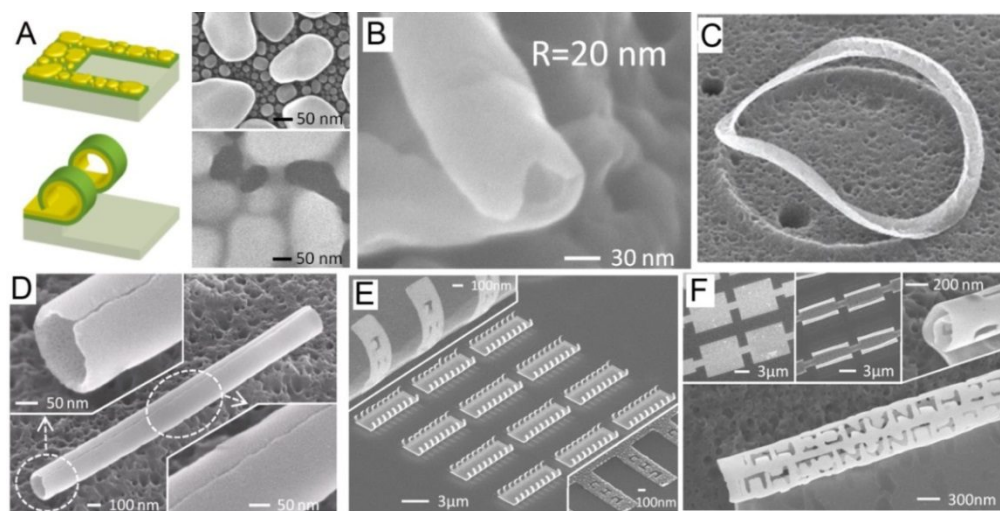


Figure 5 Self-assembly of simultaneously curved and patterned 3D nanostructures using surface forces. (A) Schematic of the process of generating strain in tin based bilayers during exothermic plasma etching of the underlying silicon. (B) Radii as small as 20 nm and (C-F) a variety of curved and patterned structures could be self-assembled. The images in panels A, B, D, E, F are reprinted from reference 81. © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. The image in panel C is reprinted from reference 82. © 2010 American Chemical Society.

assembled curved nanostructures [76, 77], but similar attempts with bilayers using strain generated by other methods such as intrinsic stress in chromium have resulted in 3D structures with only microscale radii [78-80]. In general it is fair to say that it is fairly straightforward to curve patterned thin films with micro and millimeter scaled radii, but far more challenging to curve patterned thin films with nanoscale radii.

In my laboratory, we invented a process to curve thin films with nanoscale dimensions using surface forces [81, 82] (**Figure 5A**). Here, strain was generated on inducing coalescence of a grainy low melting point tin (Sn) film, post deposition. First, bilayers composed of Sn and nickel, silicon dioxide or alumina were thermally evaporated and could also be patterned using electron beam lithography and lift-off processes on silicon wafer substrates. The patterned thin films spontaneously self-assembled during plasma etching of the underlying silicon with radii as small as 20 nm (**Figure 5B**). We attributed the strain developed in these structures to the coalescence of Sn grains. Starting with rectangular, tapered or circular planar geometries, a variety of 3D nanostructures could be formed (**Figure 5C, D**) and importantly they could also be patterned with nanoscale features with a line-width resolution as small as 10 nm using electron beam lithography (**Figure 5E and 5F**). Such nanopatterned 3D curved structures are virtually impossible to achieve using alternate methods and it is conceivable that circuits or photonic elements could be incorporated on the curved surfaces to enable a variety of new electronic and optical devices such as smart catheters and probes, waveguides and chiral optical modules. The process is also highly parallel and accessible; moreover, it is envisioned that surface forces could be used to generate such structures with alternate materials including dielectrics and semiconductors.

Self-assembly of folded nanostructures

The self-assembly of nanostructures by folding address the need for patterned devices with angled side-walls. Why do we need such structures? Firstly, as discussed and exemplified in Figure 2, the creation of patterned building polyhedral blocks is critical to the aggregative self-assembly of functional 3D electronic devices and metamaterials. Secondly, as opposed to planar modules, three dimensional patterns can elicit novel polarization dependent effects, enable the creation of 3-axis sensors that provide angular information [83], and offer the possibility for the creation of isotropic metamaterials that can be excited in the visible region of the electromagnetic spectrum.

Microscale self-folding has been an active area of research in the MEMS community since the 1990's [84, 85]. While work in other laboratories has focused on folding of structures with few panels, we invented a process to create complex 3D structures such as polyhedra (with as many as fourteen faces) using self-folding with two kinds of hinges, one of which initiates folding while the other seals the edges [86, 87]. A variety of methods had been used to fold microstructures with stressed hinges, surface forces, pneumatics and magnetics comprehensively reviewed in reference [10]. However, a central challenge was the creation of smaller sized nanostructures. In 2009, for the very first time, we described a process to fold angled structures with overall sizes as small as 100 nm; in addition to the small size of the structures, they featured side-wall patterns with a resolution of 15 nm [88] (**Figure 6**). In addition to forming nanostructures with the same materials, heterogeneous integration was also possible so that gold (Au) metal lines could be patterned on metallic or dielectric polyhedra. The possibility for heterogeneous and seamless integration with planar patterning techniques is a significant highlight of the approach. In fact, planar units could be patterned with multiple layers of conventional nanolithography so that it is conceivable that transistors or even integrated circuits could be patterned on the side walls of these nanoparticles, which would be virtually impossible to achieve by any other

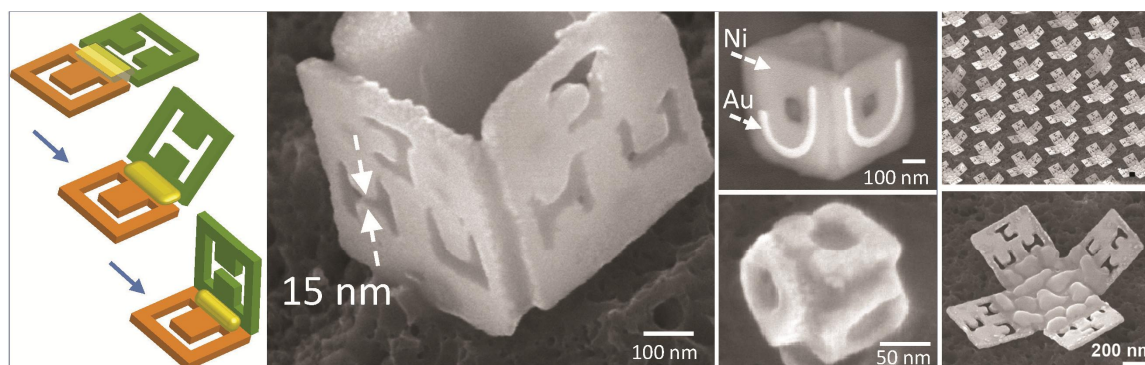


Figure 6 Self-assembly of folded nanostructures. Polyhedral nanoparticles and angled nanostructures with precisely patterned side-walls. Images reprinted from reference 88. © 2009 American Chemical Society.

methodology.

As with the curved structures described in Figure 5, this self-assembly process also occurs during plasma etching of the underlying silicon which drives coalescence in Sn hinges. In contrast, here, the Sn hinges are deposited only in select regions. The folding angle can be controlled using the processing parameters such as etch time and composition of etch gases. There is also considerable versatility in the process in terms of materials, shapes, sizes and side-wall patterns [89] (**Figure 7**). It is also noteworthy that such particles could be formed either as free-standing or arrayed structures by tuning process and etch parameters. Future challenges are the integration of transistors and more complex optical elements, the creation of ordered arrays, the extension to additional materials, and the mass production of such particles. While the self-assembly process itself is highly parallel, the multi-layer nanopatterning in 2D is typically a serial process.

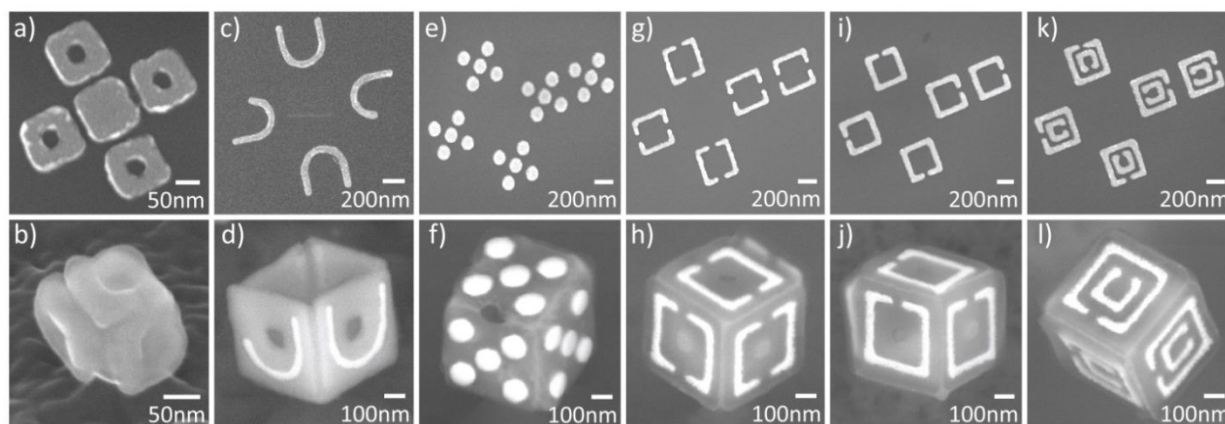


Figure 7 Versatility of self-folded nanostructures in terms of size, material composition and side-wall pattern. SEM images of the patterns and folded cubes with a–b) hollow squares, a) lithographically patterned within 13 nm thick Ni panels and b) the corresponding 100 nm folded cubic structure; c,d) 20 nm thick Au patterns defined with the alphabet patterns J, and U on 34 nm thick Ni panels; e,f) round dice-like circular 50 nm thick Au patterns on 50 nm thick Al_2O_3 panels; g,h) 50 nm thick Au twin loop split ring resonators (SRRs) defined on 50 nm thick Al_2O_3 panels; i,j) 50 nm thick Au single loop SRRs defined on 50 nm thick Al_2O_3 panels; and k,l) 50 nm thick Au double loop SRRs defined on 50 nm thick Al_2O_3 panels. Reprinted from reference 89. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Self-assembly by aggregation of nanoscale units

An important area of 3D nanofabrication is the ability to create artificial metamaterials and 3D electrical networks. Looking forward, we envision the possibility to self-assemble 3D polyhedral metamaterials and electronic crystals by aggregating the previously described nanopolyhedra patterned with optical or electronic modules (**Figure 8**). While we have self-assembled such crystals on the 100 micron scale using a hierarchical approach as shown in Figure 3, their realization on the nanoscale has yet to be demonstrated, mainly due to the need to scale up self-folding of lithographically patterned nanopolyhedra, improve yield, and develop sorting strategies to remove defective units. It is



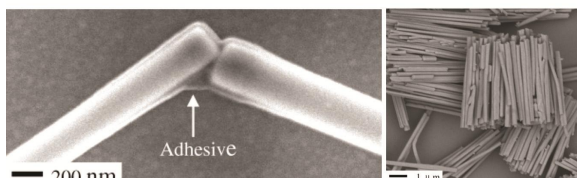
Figure 8 Conceptual schematic of the self-assembly of metamaterials with precisely patterned nanopolyhedra. Image credits: Jatinder Randhawa (Gracias Laboratory, JHU).

noteworthy that elsewhere such crystals have been formed using unpatterned cubic nanoparticles via surface interactions [90] or magnetic forces [91] which demonstrates that the realization of such materials would indeed be feasible using self-assembly processes.

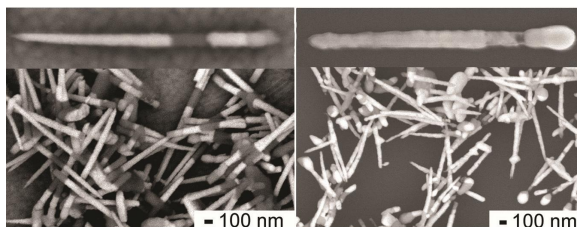
In order to create such crystals it is necessary to learn how to aggregate nanoscale units in 3D. Aggregation of nanoscale units can be achieved using a variety of methods as has been realized in the creation of photonic crystals [92], nanoparticle aggregates [93-96] or nanowire assemblies [97]. The reader is directed to several recent reviews that detail a number of methods that can be used for aggregative self-assembly of sub-micron and nanoparticles [98-103]. For example, evaporation induced crystallization of nanoparticles can result in exotic disk-like and ribbon-like architectures [104]. Capillary forces can also be utilized to create self-assemblies of nanocrystals and nanowires [105]. Fields and flows have been used to direct assembly and create photonic crystals [106] and superlattices [91]. However, one limitation for engineering practical devices is that aggregative self-assembly is often achieved using weak interactions so that the 3D structures formed are mechanically weak and could break up or fall-apart in non-aqueous media or upon mechanical deformation. Additionally, it can be challenging to form electrical connections between nanoscale units during self-assembly as would be required to form 3D electrical networks.

We have experimented with methods to form robust connections between nanoscale units using hydrophobic adhesives [107], solder [108], and diffusion bonding [109] (**Figure 9**). The assemblies themselves could be directed using dielectrophoresis [110], magnetic forces [111] or surface tension [107]. During self-assembly, the units were bonded together by adhesives, solder or the diffusing metal so that they were relatively strongly held together and the resulting assemblies resisted breakage on mild sonication. Moreover, the ability to form electrical connections between nanoscale units during self-assembly allowed 3D electrically conductive nanowire networks to be formed (**Figure 9c**), which can be a challenge [112]. Our use of solder and diffusion bonding resulted in ohmic connectivity between units, as would be required in forming 3D electrical networks by self-assembly.

A. Self-assembly of nanoscale units using hydrophobic adhesives



B. Self-assembly of nanoscale units using solder



C. Self-assembly of electrical networks using diffusion bonding

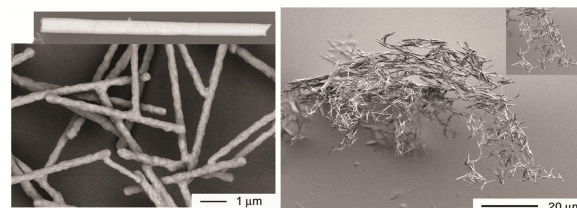


Figure 9 Strategies to self-assemble and simultaneously connect nanoscale units using adhesives, solder and diffusion bonding. The highlight of the approach is the formation of permanently bonded and electrically connected assemblies. The images in panel A are reprinted from reference 107. © 2004 American Chemical Society. The images in panel B are reprinted from reference 108. © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. The images in panel C are reprinted from reference 109. © 2007 American Chemical Society.

4. CONCLUSIONS

In conclusion, as we have shown, curving and folding of planar nanopatterns can leverage existing nanopatterning infrastructure such as electron beam lithography or nanoimprinting and take the resolution of these methods into the third dimension. Consequently we were able to assemble 3D structures with pattern line resolution as small as 10 nm in curved and angled geometries, in a highly parallel manner. Further, the aggregation of nanoscale units by self-assembly can result in photonic crystals, 3D electrical networks and metamaterials. We anticipate that these nanoscale self-assembly methods as well as the structures that they enable will find a range of applications in optics, electronics, robotics and medicine.

5. Acknowledgements

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