Design and Fabrication of Topologically Complex, Three-Dimensional Microstructures

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Two concepts for use in the fabrication of three-dimensional (3D) microstructures with complex topologies are described. Both routes begin with a two-dimensional (2D) pattern and transform it into a 3D microstructure. The concepts are illustrated by use of soft lithographic techniques to transfer 2D patterns to cylindrical (pseudo-3D) substrates. Subsequent steps—application of uniaxial strain, connection of patterns on intersecting surfaces—transform these patterns into free-standing, 3D, noncylindrically symmetrical microstructures. Microelectrodeposition provides an additive method that strengthens thin metal designs produced by patterning, welds nonconnected structures, and enables the high-strain deformations required in one method to be carried out successfully.

Building microstructures in three dimensions (3D) presents significant challenges when working with the inherently planar geometries that are accessible through projection photolithography (*1–10*). Alternatives to photolithography for fabrication of 3D structures typically use fabrication schemes that "write" patterns serially in metals and polymers—these methods either take a solid object and carve from it a structure by removal of material in a stepwise manner, or they cause localized deposition of material in a serial manner (*11–16*). Although these methods provide access to complex structures, they are often limited in the connectivities and dimensionalities of the structures they can generate. This report describes two general concepts for the design of 3D microstructures, some with complex topologies, that overcome certain of these limitations and illustrates them with simple examples. Both routes begin with a simple 2D pattern that is transferred to a cylinder and then after several steps is transformed into a 3D microstructure with noncylindrical symmetry.

One approach begins by transferring a 2D pattern onto a cylindrically symmetrical substrate (pseudo-3D). Application of an axial strain transforms this pseudo-3D structure into a truly 3D structure having a symmetry that differs from the original. To illustrate this concept, we started with a planar pattern (Fig. 1) and used it to produce a structure with cubic symmetry. A 2D structure formed from the central repeat pattern (Fig. 1C), but without hinges (weak points in the structure), would have a negative Poisson ratio: uniaxial strain applied in the *x* direction would cause expansion of the structure in the *y* direction in the plane of the structure (*17*). If hinges (thinner wires at joints) and rigid sections (hexagonal mesh) are introduced, however, the dimensions of the structure are constrained in the *y* direction and the strain is transferred evenly to the structure. For the 2D structure to relieve applied strain, the rigid edges of the cube would bend at the hinges, and the wire (Fig. 1C, asterisk) would move out (either up or down) of the plane of the structure. Once this structure is projected into three dimensions—that is, the design is transferred to a cylinder—points A all lie in one plane and points B lie above this plane. When axial strain is applied, the rigid hexagonal mesh constrains points A in the plane of the cylinder, and points B must move further up (and out) of the plane to relieve the applied strain.

Patterning cylinders and other curved substrates, using soft lithography (*18*) and in particular microcontact printing (μCP), has made it practical to produce structures with features as small as a few micrometers (*19–21*). Microcontact printing on a silver-coated capillary (*22*) (Fig. 1), using a stamp (*23*) molded in this 2D pattern (Fig. 1C), followed by wet-chemical etching (*24*), electrodeposition of metal, and dissolution of the substrate resulted in the formation of a self-support-

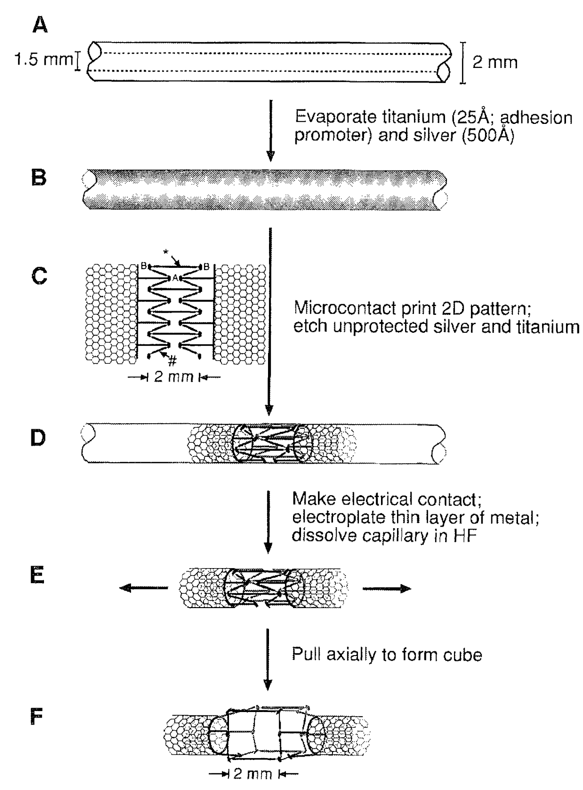

Fig. 1. Schematic illustration of the fabrication of 3D structures formed by deformation of a cylindrical mesh under tension. Using an electron-beam evaporator, we coated glass capillaries (~ 2 mm diameter) (**A**) with titanium (~25 Å; adhesion promoter) and silver (~500 Å). Two orthogonally rotating stages ensured that the capillaries were evenly metalized around their circumference (*20*) (**B**). Microcontact printing of hexadecanethiol with an elastomeric stamp formed a patterned self-assembled monolayer on the capillary. The geometry of the stamp is illustrated in (**C**); the dimensions and angles of the wires that form the cube were adjusted relative to the circumference of the cylinder: for a cube with edges of length *d* formed on a cylinder with a diameter, *d*, the edge of the cube (*) was set equal to *d*, the components of the edges (#) were of length *d*/2 and were oriented at an angle of 52° to the edge *. Immersion for 15 to 30 s in an aqueous ferricyanide bath (0.001 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, 0.1 M $Na_2S_2O_3$) removed the underivatized silver and ~10 s in 1% HF solution removed the exposed titanium. A conductive metal pattern was formed in the design of the stamp (**D**). Electroplating a thin (~20 μm) layer of silver from a plating bath held at room temperature (Technic, Providence, RI, Techni-Silver E2) at a current density of ~20 mA/cm² increased the rigidity of the structure. We estimated the area of the pattern by measuring the total area spanned by the pattern and then calculating, based on the design, the percentage of the area covered by metal. Dissolution of the underlying glass substrate in HF produced a free-standing mesh (**E**). (Caution: direct exposure of skin to concentrated, aqueous HF can damage skin and bones.) The final cube formed when the mesh was expanded under tension by pulling on both ends of the structure with tweezers. Further electroplating reinforced the structure and made it rigid (**F**).

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ing, metallic mesh with a negative Poisson ratio (Fig. 2A). Application of axial strain to the mesh (by pulling the ends of the structure in opposing directions) caused the structure to "pop" into the cube shape; this deformation occurred with controlled bending at the hinges (25). Three adjacent cubes formed by this procedure are shown (Fig. 2B). These cubic structures illustrate the possibility of transforming planar designs into 3D, noncylindrically symmetrical microstructures. This type of approach is applicable to more complex geometries, although the designs that provide and concentrate the required strain must be explored. At smaller feature sizes, it potentially could be used to produce components with negative Poisson ratios that could function as compliant microgrippers or micropositioners. The rapid prototyping technique (26) that we used to make stamps determined the feature sizes of our structures. Substantially smaller structures could certainly be made with stamps formed from masters produced by conventional photolithography—a free-standing hexagonal mesh with features as small as about 8 μm is shown (Fig. 2C). Registration at smaller scales will become critical—we have shown that we can adjust the relative orientation of the stamp and substrate to within 0.1°, so it should be possible to align features to within 2 μm on a 125-μm-diameter substrate (20).

The second concept for fabrication produces 3D microstructures with complex topologies from a 2D pattern. This approach uses electrochemical deposition of metal to bridge patterns at the intersection of two (or three) planes. Given that the intersection of two planes defines a line, the topological complexity of structures that can be fabricated is increased by designing features that interact along this line. For example, in a planar geometry, three links projected onto a planar surface cannot be joined together with multiple, unconnected crossing points (without cutting them). At the intersection of two planes, however, these three links can be placed so that they maintain their individual structure but are linked to form a linear chain (Hopf links) (Fig. 3) (27, 28). Bringing two rectangular rods together along their edges (Fig. 3E) is topologically equivalent to intersecting two planes, as is bringing two parallel cylinders together at a tangent line—these junctions define lines around which fabrication can be performed.

To demonstrate this concept, we transferred a pattern of half-links (Fig. 3C) into a layer of photoresist coated on a metalized glass capillary using a flexible photomask (26). Two patterned capillaries were aligned (to form the topological equivalent of two intersecting planes) and secured in place, with their patterns matched to form the template for an interlinked chain. Isotropic electrodeposition of nickel in the regions where the underlying metal was exposed (that is, the half-links) produced electrochemically welded, interconnected nickel links. The release of the structure from the underlying support produced a linear, interlinked chain (Fig. 4).

Many connectivities are possible using intersecting planes for fabrication: multiple planes can be caused to intersect along a line; multiple cylinders can be contacted along multiple parallel, tangent lines; three or more planes can be made to intersect at a point to increase further the complexity of accessible structures [trefoil knots or Borromean Rings (27, 28) are possible]. Smaller structures should be possible but aligning the relevant planes becomes increasingly difficult.

These alternative concepts for microfabrication offer strategies for making 3D microstructures with complex topologies. Both methods take advantage of the ability of microcontact printing and other soft lithographic techniques to pattern cylinders by using 2D patterns embossed in the

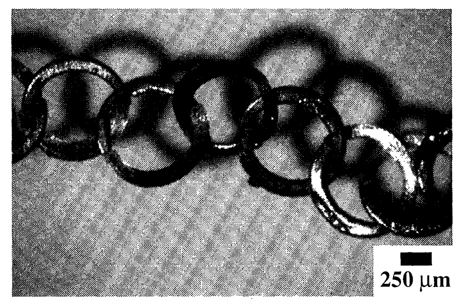

Fig. 4. Optical micrograph of a free-jointed nickel chain formed by the procedure shown in Fig. 3. The final thickness of nickel was ~50 μm.

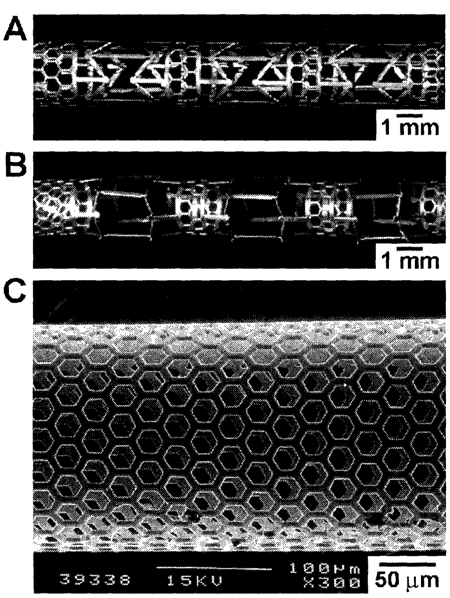

Fig. 2. Photographs of a free-standing, cylindrical, unexpanded silver mesh patterned in the design of the projected cubes (as shown in Fig. 1) (**A**) and three expanded cubes (**B**) formed by μCP followed by electroplating and deformation under tension. (**C**) Scanning electron micrograph of a free-standing, cylindrical, hexagonal mesh formed by μCP followed by electroplating.

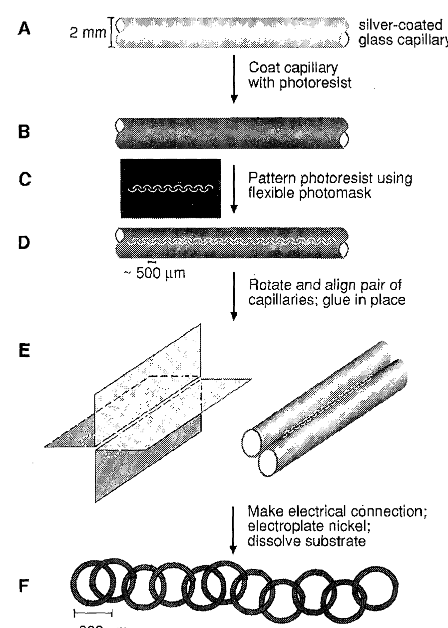

Fig. 3. Scheme for fabricating a chain using a flexible photomask and electrochemical welding. By pulling metallized glass capillaries (**A**) slowly (~1 cm/min) from bulk solution, we coated them with photoresist (Shipley 1813, Microlithography Chemical Corporation, Newton, Massachusetts) (**B**). Capillaries were hard-baked at 105°C for ~3 min. Exposure (~8 s) of the coated capillary to ultraviolet light (using a Karl Suss mask aligner) through a flexible mask [design shown in (**C**)] wrapped around its surface transferred an appropriate pattern into the photoresist (**D**). Under an optical microscope, we aligned two patterned capillaries so that they were in close proximity to one another and their patterns matched to form a chain (**E**). (Links correspond to openings in the photoresist. Dotted lines represent links on the undersides of the capillaries that are not visible from the top.) Electroplating nickel, from a nickel sulfamate-based plating bath (Technic, Providence, Rhode Island, Techni-Nickel "S") held at 45°C for ~30 min at a current density of ~20 mA/cm², in areas defined by the photoresist electrochemically welded together the ends of the chain links. We released the freely jointed chain from the capillaries by dissolving the photoresist in acetone, the silver in an aqueous ferricyanide bath, and the titanium and glass in concentrated HF (**F**).

surface of elastomeric stamps or flexible photomasks. Subsequent processing steps transform patterns on these cylindrically symmetrical substrates into structures with different symmetries and more complex topologies. Microelectrochemistry provides an additive method that strengthens thin metal patterns produced by printing and etching and that welds proximal, nonconnected structures. Potential applications for these techniques may be in the fabrication of ultralight structures for micro air and space vehicles, components for microelectromechanical systems, 3D metallic membranes and electrodes, and, at smaller dimensions, dielectric structures for photonic band gap materials.

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23. A rapid prototyping technique allowed flexible photomasks to be generated quickly [D. Qin, Y. Xia, G. M. Whitesides, *Adv. Mater.* **8**, 917 (1996)]. We used a computer-aided design program (Macromedia Freehand) to design patterns. Designs were printed onto transparencies with a commercial laser-assisted image-setting system (Herkules PRO, 3386 dpi, Linotype-Hell Company, Hauppauge, NY). The resolution of the printer limits the smallest feature size to about 20 μm. These flexible transparencies served as photomasks for photolithography. Elastomeric stamps were prepared by casting polydimethylsiloxane against a master created by performing photolithography with a flexible photomask.
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From Shifting Silt to Solid Stone: The Manufacture of Synthetic Basalt in Ancient Mesopotamia

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Slabs and fragments of gray-black vesicular "rock," superficially resembling natural basalt but distinctive in chemistry and mineralogy, were excavated at the second-millennium B.C. Mesopotamian city of Mashkan-shapir, about 80 kilometers south of Baghdad, Iraq. Most of this material appears to have been deliberately manufactured by the melting and slow cooling of local alluvial silts. The high temperatures (about 1200°C) required and the large volume of material processed indicate an industry in which lithic materials were manufactured ("synthetic basalt") for grinding grain and construction.

Lacking basic raw materials such as stone, metal ores, or large timber, the ancient inhabitants of southern Mesopotamia used the one natural resource they possessed in abundance, alluvial silt, for pottery, architecture, writing materials, objects of art, and even tools such as sickles. The evidence presented here, however, demonstrates that they also converted silt into a material that in color, texture, and mechanical properties is similar to natural vesicular basalt—that is, a hard, durable, useful substitute for stone that could be used for such purposes as grinding grain.

A surface survey (*1*) conducted at the early second millennium (*2*) B.C. site of Mashkan-shapir suggested that some of the overfired material that litters Mesopotamian sites might not be kiln debris. Several large, rectangular (about 80 cm by 40 cm by 8 cm) slabs were found near the remains of the main temple in Mashkan-shapir (Fig. 1). One of the two large sides of each was flat, with the opposite face uneven. The material resembles basalt, but the uniform size, shape, and characteristic appearance of the slabs suggest that they are not naturally formed rock. They appear to be the result of deliberate manufacture and not an accidental by-product of some other manufacturing process.

At Mashkan-shapir, these slabs were only found in the southern, religious quarter, but their characteristic profile, with uneven top and flat bottom surfaces (Fig. 2), can be used to link them with several hundred fragments found across the site. The large slabs and fragments were around 8 cm thick, except where the latter had been worn down by grinding. Except where broken, the edges show evidence of deliberate trimming. Closest to the flat face, the vesicles are small (0.1 to 0.5 mm), and they increase in size as they approach the uneven face (2 to 3 mm). The pieces are black to dark gray in color except for the uneven surface, which usually exhibits a greenish tinge. Compositionally, this material falls outside the range of known basalts (*3*), particularly in the high CaO and K_2O concentrations and low amounts of Al_2O_3 and total Fe, but is similar to the composition of a sample of alluvial silt from the area (Table

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