Three-Dimensional Metallic Microstructures Fabricated by Soft Lithography and Microelectrodeposition

Rebecca J. Jackman,[†] Scott T. Brittain,[†] Allan Adams,[‡] Hongkai Wu,[†] Mara G. Prentiss,[‡] Sue Whitesides,[§] and George M. Whitesides*,[†]

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, Department of Physics, Harvard University, 9 Oxford Street, Cambridge, Massachusetts 02138, and School of Computer Science, McGill University, 3480 University #318, Montreal PQ H3A 2A7, Canada

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Soft lithography offers a convenient set of methods for the transfer of patterns to planar and nonplanar substrates. Microelectrodeposition can transform thin metal patterns into self-supporting microstructures, weld components together, and strengthen microstructures after deformations. Together, soft lithography and electrochemistry provide synergistic technologies and the basis for a strategy for converting planar patterns into three-dimensional (3D) microstructures with complex topologies. This strategy is illustrated in the formation of folded tetrahedra, square-based pyramids, cylinders with joints, "pop-up" cubes, and linked chains and knots.

Introduction

This paper describes three approaches that we have taken to microfabrication of metallic, three-dimensional (3D) structures. All of these methods combine soft lithography and microelectrochemistry to transform two-dimensional patterns into three-dimensional microstructures. Microelectromechanical systems (MEMS) and other miniaturized systems (for example, stents and metallic prostheses, and small air vehicles) require functional, 3D metallic components with elements having dimensions from 1 μm to 1 mm. For large structures, well-established techniques exist for shaping metal components: for example, casting, rolling, forging, stamping, grinding, milling, and cutting. Nuts and bolts, rivets, glue, and welding join these components. Performing most of these operations on micron-scale components is, however, difficult or impossible: practical solutions to the fabrication of metal structures with micron-scale components will require new approaches *not* drawn from existing technologies.

Electroforming (electrodeposition and electromachining) is a technique that scales down well. Electroplating metal onto an appropriately shaped mandrel and then separating the plated metal part from the mandrel is an accepted technique for the fabrication of some types of metal components.[1] On the basis of the broad generality of the techniques reported here, and described by others elsewhere,[2−5] we believe that microelectrochemistry will be central to shaping metals at the micron scale and in joining them to produce 3D microstructures. Electrodeposition can (i) transform thin (~500 Å) structures into self-supporting microstructures, (ii) weld components together, and (iii) make it possible to use deformations to shape the microstructures to produce 3D structures by repairing any strain-induced defects with electrodeposition of additional metal over the damaged areas.

Most techniques that are used in conjunction with electrochemical methods to produce micron-sized structures have developed from existing processes in microelectronics and are inherently planar.[6] Specifically, metal microstructures are usually made by through-mask electroplating[2,4] or LIGA (*Lithographie, Galvanoformung, Abformung*—Lithography, Electroplating, and Replication).[7−9] Examples of functional structures formed by these techniques are thin-film magnetic read−write heads,[10] X-ray lithography masks,[11] bubble memory devices,[11] thin-film chip carriers,[2] and components for MEMS (nickel turbine rotor,[5] magnetic microactuator,[12] microgears, microvalves and pumps,[13] capacitive accelerometers,[14] microtransformers[15]).

While these methods can form high-aspect-ratio microstructures, it is difficult to introduce the variation in

* To whom correspondence should be addressed.
[†] Department of Chemistry and Chemical Biology, Harvard University.
[‡] Department of Physics, Harvard University.
[§] School of Computer Science, McGill University.

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the dimension out of the plane of the substrate that is needed to produce topologically complex, 3D microstructures. Full three dimensionality either is introduced layer-by-layer or requires different techniques that serially carve microstructures from solid objects by laser micromachining,[16,17] or "write" 3D microstructures in metals.[18−20]

Our approach to the fabrication of 3D metallic microstructures has been to couple soft lithographic techniques[21] with microelectroplating, both through a mask of photoresist and onto isolated conducting structures.[22] Soft lithography uses an elastomeric or flexible element in the pattern-transfer step; this element permits the formation of high-resolution features in metal or photoresist (on a conductive substrate) on both planar[23−25] and nonplanar substrates.[26] Specifically, we use microcontact printing to form patterns in the metal, and we use a flexible photomask, formed by rapid prototyping,[27] to produce patterns in the photoresist. These features then direct the deposition of metal during the electrodeposition step.[28] We have developed three strategies for fabricating 3D microstructures using these techniques: (i) we print a pattern of a nanometer resist on a planar metalized substrate, etch the unprotected metal, and electrodeposit additional metal to form a self-supporting structure and, then, after release of the structure from this substrate, deform it to convert the 2D pattern into a 3D structure; (ii) we use an elastomeric stamp bearing a 2D pattern to print a pattern onto cylindrical substrates and then electroplate metal onto this pattern, after etching the unprinted regions, to give the structure rigidity and ductility so that, after its release from the substrate, it will deform under an applied stress into a more complex structure; and (iii) we pattern photoresist on a cylindrical substrate, using a flexible photomask, and use electrodeposition to create topologically complex microstructures.

Results and Discussion

Producing Metallic Structures on Planar Substrates Using Through-Mask Electroplating and Soft Lithography. Figure 1 illustrates two methods for producing planar metallic microstructures using microelectrochemistry. The first method (Figure 1A) is developed from microelectronics and is referred to as through-mask electroplating or LIGA (if X-rays from a synchrotron source are used). It involves patterning of a layer of photoresist formed on a conductive substrate with UV or X-ray light using an appropriate mask, with an electron beam. Developing the photoresist removes the activated areas (for a positive resist) and re-exposes regions of the conductive substrate. With this substrate as the cathode in a plating bath, metal deposits electrochemically into the mold defined by the photoresist. Removal of the photoresist and release of the metallic structure from the substrate generate a free-standing 2D microstructure with sidewalls defined by the photoresist.

The second method (Figure 1B) to produce metallic microstructures starts by using microcontact printing (μCP) to pattern features that are routinely as small as a micron on a conductive substrate (usually, silver or gold).[25] It uses an elastomeric stamp to transfer an "ink" to specific regions on a substrate. The ink either prevents removal[23,29] or initiates deposition[30] of material. In this paper, we apply this technique using hexadecanethiol (HDT) as the ink that forms a self-assembled monolayer (SAM) on silver; this SAM serves as a resist against etching. Once silver and titanium (an adhesion promoter for the film of silver) have been removed from unprotected regions of the substrate by wet-chemical etching, the thin, conductive, patterned silver structure that remains can direct electrodeposition. We made electrical connection to the structures using silver epoxy and then placed them into a commercial plating bath as the cathode. Typically, we deposited silver or nickel, but many other metals can be electrodeposited.[31,32] Again, dissolution of the substrate produced free-standing, 2D structures.

When forming structures by this technique, there are are two possible reasons why the feature on the stamp and the final feature will differ in size: the printing step and the electrodeposition step. We estimate that the spatial errors in the size of the printed components are small: printed features are typically within $\pm$2% of the size of the features on the stamp. A previous investigation of the errors in the registration of patterns produced by μCP with a compliant PDMS stamp measured distortions on the order of $\sim$500 nm over square areas of $\sim$0.25 cm^2, for stamps similar to the ones used here; these distortions can be reduced further by using thin ($\sim$0.1 mm) stamps cast against rigid supports.[33] During the electroplating step, the growth of the structure is approximately isotropic and results in a structure with rounded side walls. It is this step that accounts for the majority of difference between the size of a pattern on a stamp and the size of a feature in a free-standing metal structure. The exact width of the final 3D microstructure depends on the width of the printed pattern and the final thickness of the electroplated 3D structure. For example, if a feature $\sim$25 μm wide is printed, once the structure has been plated to a thickness of $\sim$25 μm, the features will now be $\sim$75 μm wide. The difference between these dimensions, however, is predictable and could, to some extent, be compensated for in the design of the stamp used for printing. Other groups have taken advantage of this isotropic growth during electroplating to generate structures with controlled profiles.[34]

The combination of μCP and electrodeposition has

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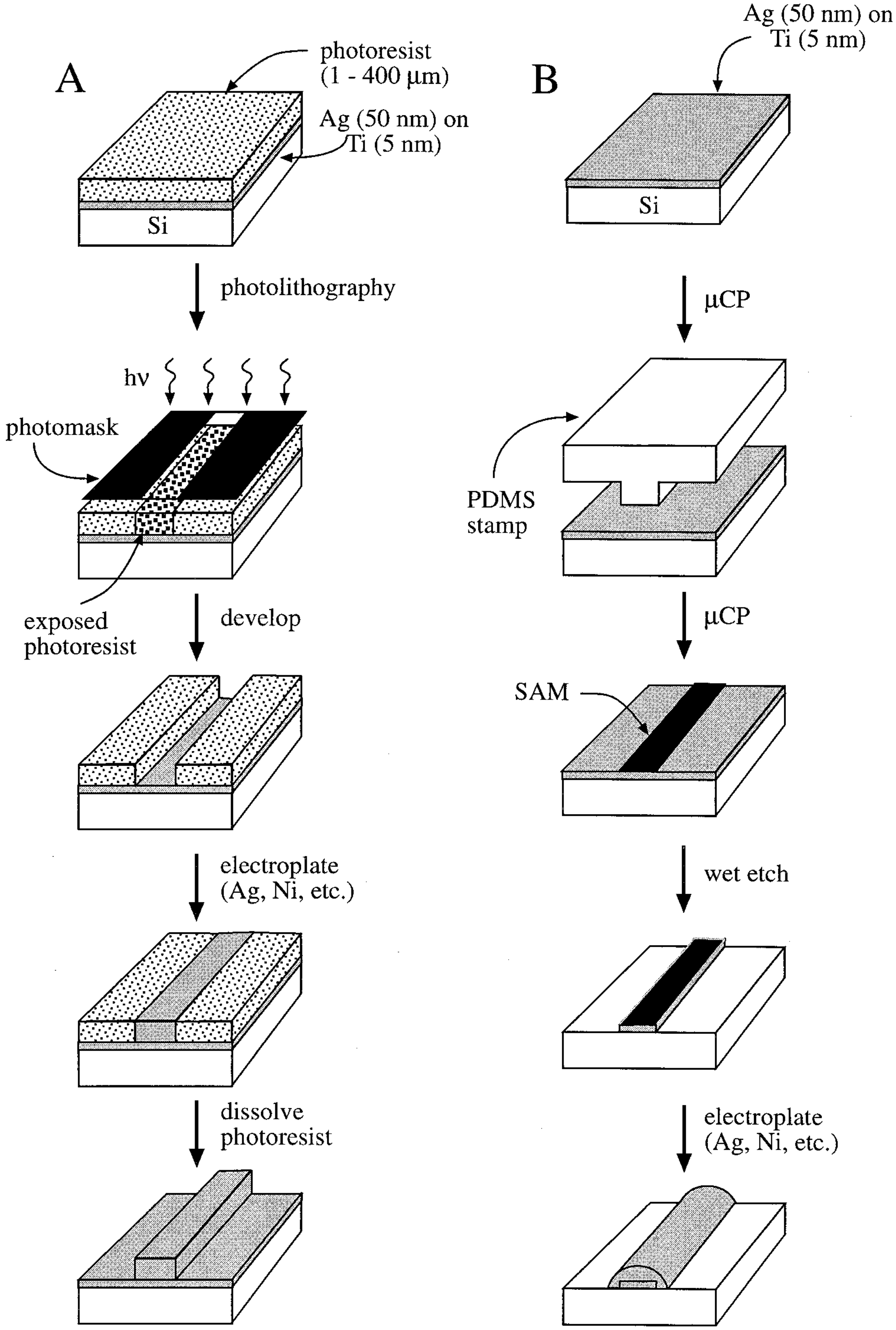

Figure 1. Two methods for producing metal microstructures on planar substrates using electroplating. (A) Through-mask electroplating or LIGA. We coated a thin gold or silver film with a layer of photoresist. Exposure of the photoresist to UV light through a patterned photomask altered chemically the exposed regions. These regions dissolved when treated with a developing solution. The remaining photoresist prevented electrical contact between the underlying areas of metal film and an electroplating solution: metal electrodeposited selectively into the uncovered regions of the silver film. The edges of the photoresist constrained the growth of the metal deposit and determined the shape of the sidewalls of the final metal structure. Dissolution of the photoresist in an organic solvent revealed the electroplated structure. (B) Microcontact printing and electroplating. We deposited thin layers of Ti (50 Å, used as an adhesion promoter), followed by Ag (500 Å), onto substrates (Si wafers, glass slides). A PDMS stamp "inked" with a 1 mM ethanolic solution of hexadecanethiol, $CH_3(CH_2)_{15}SH$, made conformal contact with the silver surface and transferred the thiol to the surface. The regions of the silver film covered with the SAM resisted subsequent wet etching with an aqueous ferricyanide solution. The remaining silver pattern acted as the cathode in an electrochemical cell, and metal (Ag, Ni, and others) electrodeposited isotropically from solution onto this electrode.

several advantages over through-mask electroplating: it uses only an elastomeric stamp in the pattern-transfer step, so routine clean room access to perform photolithography is not necessary; it is a simple procedure that requires basic equipment and is therefore inexpensive; a single stamp can be used many times (photoresist molds can be used only once); and it (and other soft lithographic techniques) can be used to pattern nonplanar and curved substrates.

Producing Metallic Structures on Cylindrical

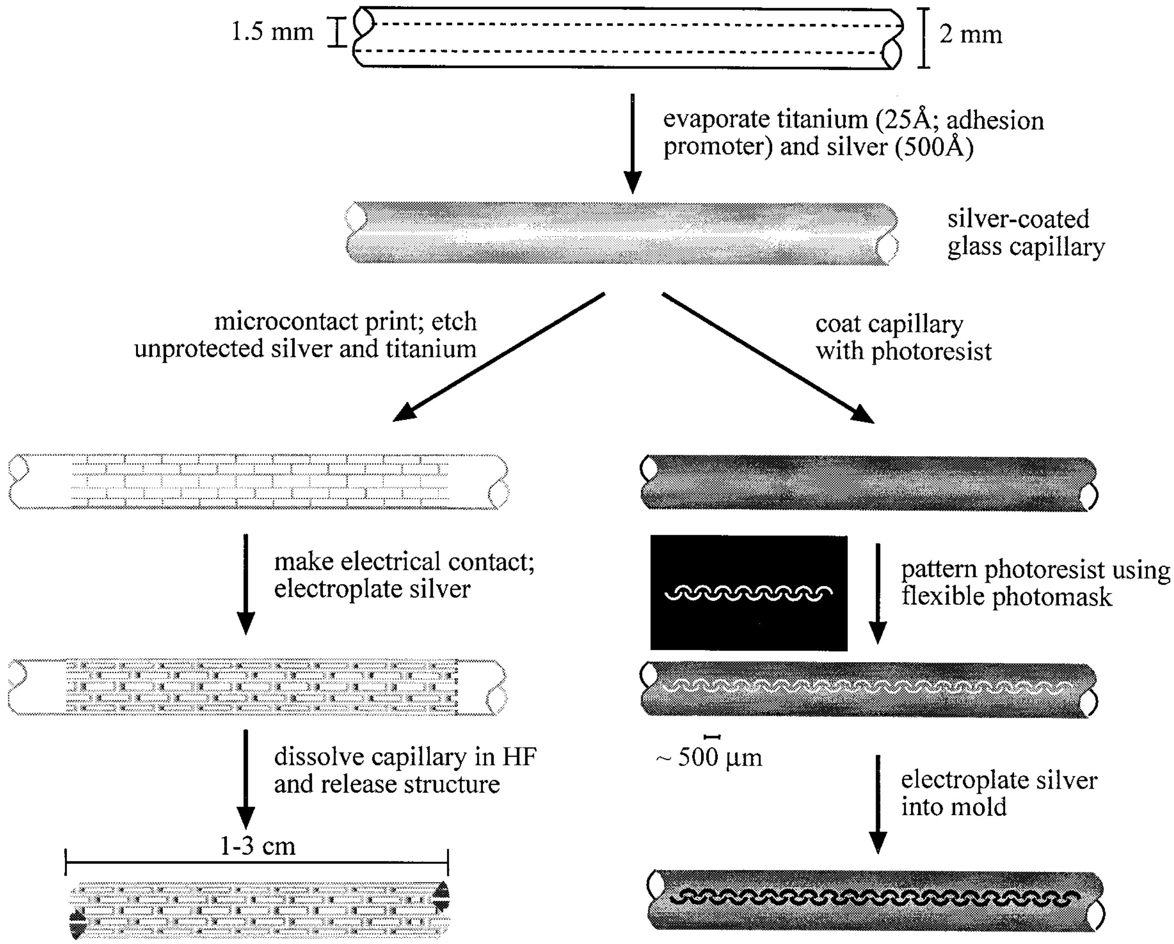

Figure 2. Scheme illustrating the use of soft lithographic techniques and electrodeposition to pattern cylindrical substrates. Using an e-beam evaporator, we coated glass capillaries (~2 mm diameter) with titanium (25 Å; adhesion promoter), followed by silver (500 Å).[38] (A) Microcontact printing (μCP). Microcontact printing hexadecanethiol using an elastomeric stamp in three-dimensional bas relief on its surface, followed by wet-chemical etching of the unprotected silver and titanium, formed a continuous, conductive metal pattern in the design of the stamp. The thin silver pattern served as the cathode in an electroplating bath. After electroplating, dissolution of the capillary in aqueous HF (49%) produced a structurally sound microstructure. (B) Flexible photomask. We coated a metalized glass capillary with photoresist by pulling it slowly from a bulk solution. Exposure of the coated capillary to UV light through a flexible photomask (produced by rapid prototyping) wrapped around its surface transferred an appropriate pattern into the photoresist. After removing the exposed photoresist in a developing solution, the substrate was used as the cathode in an electroplating bath, and metal deposited into the mold defined by the photoresist.

Substrates Using Soft Lithography. The use of photolithography (which is inherently planar) and e-beam lithography (which is a serial technique) limits traditional through-mask electroplating to the fabrication of 2D microstructures with high aspect ratios. Patterning cylindrical substrates has been accomplished using an e-beam system modified with a stage that allows the rotation and translation of a fiber during the writing step[35] and using a lathe to control the orientation of a cylinder relative to an X-ray mask and source.[36] The equipment required for either of these techniques makes them inaccessible to most researchers. We have developed two simple soft lithographic techniques—microcontact printing (μCP) and the use of flexible photomasks—that we use in conjunction with microelectrodeposition to produce patterns on cylindrical microstructures (Figure 2). In both cases, it is the mechanical flexibility of the pattern-transfer element—an elastomeric stamp or a flexible transparency—that allows the patterning of cylindrical substrates.

Microstructures formed by microcontact printing on cylindrical substrates (Figure 2A) have applications as photomasks for the generation of in-fiber gratings,[37] as microinductors[38] and microtransformers,[39] and as coronary stents.[28] These structures were produced by rolling the cylindrical substrate across the surface of an elastomeric stamp.[37] During the pattern-transfer step, the substrate and the stamp come into conformal contact, and ink—the alkanethiol—transfers from the stamp to the metal surface. After wet-chemical etching to remove the underivatized metal, we electroplate metal and then remove the underlying substrate. We have shown previously that microcontact printing when used with electrodeposition can produce cylindrical meshes (diameter ~200 μm) with feature sizes (after electroplating) of less than 8 μm.[22]

Electrodeposition coupled with the use of flexible photomasks (Figure 2B), formed by rapid prototyping[27] to pattern cylindrical substrates, serves as the nonplanar

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equivalent of through-mask electroplating. Once a conductive substrate has been coated with photoresist, it is exposed to flood UV light through a flexible mask wrapped around its exterior. A pattern in the photoresist results in development of the exposed resist and directs the deposition of metal during an electroplating step.

Patterning with μCP and flexible photomasks are complimentary techniques for producing features on curved substrates (as are μCP and through-mask electroplating on planar substrates). The application of μCP and electrodeposition to the fabrication of microstructures is only possible when the microstructure is continuous. If the desired structure is not continuous—that is, if sections of the structure are electrically isolated from one another—it can be printed by μCP, but only connected sections will plate during the electrodeposition step. A flexible photomask does, on the other hand, allow the fabrication of discontinuous structures because the continuous metal layer that lies under the patterned photoresist ensures that the entire substrate is conducting and can be held at the potential used for electroplating.

Microelectrochemistry Enables the Application of High-Strain Deformations To Produce Three-Dimensional Microstructures. By electroplating ductile metals (e.g. silver, gold) onto thin metallic structures formed by μCP (followed by wet-chemical etching) or by using a flexible mask, we can provide the rigidity necessary for microstructures to be self-supporting—the metal layer deposited by evaporation is too thin (typically only ~50 nm) for this purpose. The plating step also ensures that the structures will yield, but not break, under an applied strain. This property permits us to perform initial fabrication steps on a substrate that is relatively easy to pattern (that is, a planar or cylindrical substrate), using an appropriate design, and then subsequently apply a force to the structure that deforms it into the desired 3D structure. This structure may have cracks, small tears, or stress-thinned regions resulting from high-strain deformations. Electrodeposition of additional metal on the structure covers and partially fills these defects and largely repairs the mechanical properties of the structure.

(a) Transformation of Planar Structures into 3D Structures by Folding (Micro-origami). Many simple three-dimensional structures—that is, tetrahedra, cubes, dodecahedra—are relatively easy to fabricate: we can unfold these structures onto a plane (2D). We combined rapid prototyping[27] with a molding step to produce a stamp with the 2D design of interest in relief on its surface. After μCP and etching, we electrodeposited metal onto the 2D structure, to provide it with some rigidity, released it from the substrate, folded it, and electroplated the folded structure to produce a three-dimensional microstructure. Figure 3A shows a diagram of a tetrahedron unfolded and projected into two dimensions and an optical micrograph of a folded tetrahedron after electroplating. A series of tabs and slots, arranged around the sides of the tetrahedron, held the sides of the folded structure in the correct locations during electroplating.

(b) Transformation of Planar Structures into 3D Structures by Out-of-Plane Deformations. The introduction of components into a 2D pattern that will deform in a controlled manner under tension allows the construction of 3D structures. Examples are hinges that are formed from thinner sections of metal that will bend and expandable sections, for example, zigzag lines (the 2D equivalent of a coil), that will straighten under tension. Figure 3B illustrates a design for a microstructure having components that deform on the application of an out-of-plane deformation. By pulling the crossing point of the two zigzag lines out of the plane of the square support, the zigzag wires straighten and a square-based pyramid results. This figure also shows an optical micrograph of an undeformed, 2D microstructure and an adjacent structure that has been deformed to produce the pyramidal structure. The ductility of the plated metal (silver) enables the application of high-strain deformations while keeping cracking to a minimum; we can use electrochemistry to strengthen the deformed structure and to repair small cracks.

We demonstrated both concepts for 3D fabrication from planar structures at a scale where the smallest printed features were ~25 μm. This scale was convenient because it allowed the formation of stamps by rapid prototyping[27] and the application of deformation (folding or out of plane stretching) easily by hand. At smaller scales (for example tetrahedra with sides < 1 mm), different strategies for the construction of 3D microstructures from self-supporting planar structures will be necessary, for example, structures designed to fold spontaneously on release from a substrate[40,41] or larger arrays of 2D structures to which out-of-plane deformations can be applied that will erect all components of the array simultaneously.

(c) Introduction of Deformable Components into Cylindrical Structures. While only certain 3D structures map onto a 2D representation (previous sections), *all* cylindrical patterns can unfold onto a planar surface. Conversely, using a planar design, we can, in principle, produce a stamp for microcontact printing that we can use to print a desired pattern onto any cylindrical substrate. As with planar metallic structures, the application of a deforming force to a free-standing, metallic, cylindrical structure can change its shape and symmetry. By designing the structure appropriately, when we apply radial or axial strain to the cylinder, or when we bend it at a predesigned weak point, we produce a 3D structure that could not have been printed directly.

As an example, we have designed components in cylindrical meshes that can be used to control the location and orientation of bending (Figure 4). For a lightweight, rigid cylindrical mesh structure without deformable components, bending the structure would cause the mesh to collapse. We introduced a joint that consisted of two open diamonds arranged on opposite sides of the capillary. A single diamond would also have allowed the structure to bend but would have offered less control over the degree and orientation of bending. These structures were designed to allow a bend of at least 90 ° to be introduced into the structure. As the joint was deformed manually by moving the two vertexes of one diamond (marked * and that are not directly connected to the rigid sections) out relative to the axis of the capillary using a pair of tweezers (indicated by the solid arrows), the other two vertexes (and the attached rigid sections) moved together (as indicated by the dashed arrows in Figure 4B). The diamond on the outside of the joint deformed slightly in the opposite sense and provided a limit on the angle of bending. We bent the protruding points of the diamond on the inside of the joint back toward the other diamond and electroplated the joint further to weld it in place (Figure 4C and D). The relative positioning of adjacent pairs of diamonds on the cylinder controls the relative orientations of the rigid sections of capillary; for example, if we were to print a pattern where each pair of diamonds between each rigid section was slightly rotated relative to the previous pair, the structure, after bending, would form a helix.

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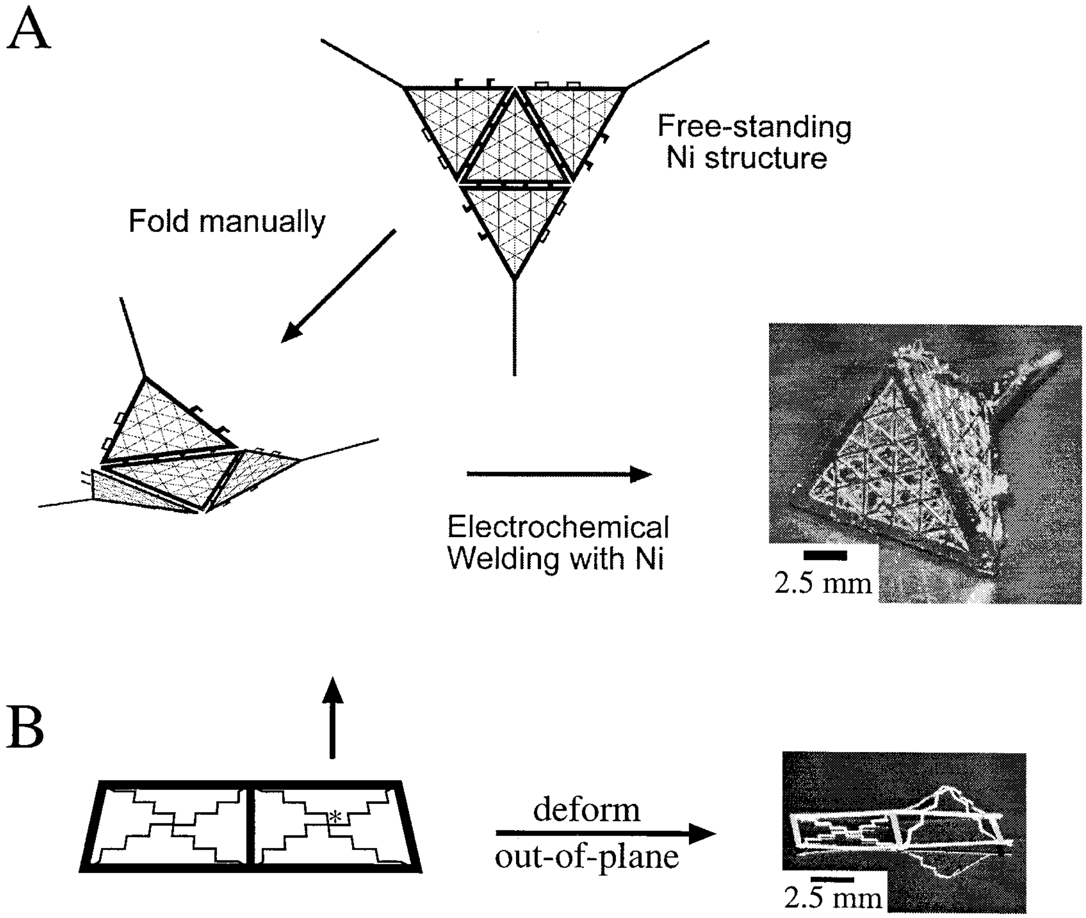

Figure 3. (A) Planar design fabricated by μCP on and wet etching of a silver film, followed by electroplating of nickel. Dissolution of a sacrificial SiO_2 layer (not shown) with aqueous HF released the metal grid from the silicon substrate. Manual folding of the grid resulted in a tetrahedral structure. A system of tabs and slots held adjacent edges in close contact during a final electrochemical welding step. (B) Transformation of a planar structure into a 3D structure by controlled deformation. We formed a self-supporting, 2D microstructure (see pattern) by μCP, followed by etching, then electrodeposition, and, finally, release from the substrate (see Figure 1A). We designed the thin, zigzag lines to deform (straighten) and the thicker, square outline to withstand deformation and maintain a square base. The optical micrograph shows an undeformed, 2D metallic microstructure and a similar structure after the out-of-plane deformation. The deformation produced a square-based pyramidal structure. Further electroplating increased the structural integrity of the 3D microstructure.

(d) Transformation of Cylindrical Structures into Noncylindrical, 3D Structures by Applying Axial Tension. Although the introduction of joints into a cylindrical structure allows the fabrication of a 3D structure that could not have been printed directly using a stamp (see previous section), we must apply a small force to each joint individually to deform the structure. An alternative strategy for this approach to 3D microfabrication is to design structures to which an applied macroscopic force will be distributed among a large number of small, deformable components that will move to give rise to a new 3D structure. For example, a radial deformation, produced by inserting a microballoon into a cylindrical microstructure and inflating it, will cause radial expansion;[28] the structure will, however, remain cylindrically symmetrical if it is unconstrained during expansion. Here, we demonstrate that the application of an axial deformation, by applying tension to an appropriately patterned cylindrical substrate, can cause a transformation into a noncylindrical structure.

Figure 5 shows a 2D pattern designed for printing onto a cylindrical substrate and also to deform under axial tension. Rigid regions in the design (the hexagonal mesh) that do not deform under tension allow the applied macroscopic force to be transferred to the wires of the structure. The use of weak points, or “hinges”, in the structure (i.e. sections of wire at the corners of the structure that are thinner than those along the edges of the cube ($\sim$25 μm versus $\sim$100 μm)) allows the structure to deform radically under stress without bending the rigid rods (which form the sides of the cube). Using these hinges to limit the deformations to predetermined points allowed us to predict the deformation of a structure under tensile stress.

Figure 5A illustrates a pattern designed to deform under tension. Application of tension causes deformation at the hinges (*A*, *B*, *C*, *D*). The rigid rods connecting the hinges serves as levers. The angle *ABC* is fixed (by design), so tension causes the point *B* to move out of the plane (either up or down). When this pattern is projected onto a cylinder, the point *B* is already out of the plane of *A* and *C*, so that when tension is applied, the point *B* moves further *out* relative to the axis of the cylinder—it is not able to move in. The structure shown in Figure 5B that we used to pattern a cylinder worked using the same principle—when axial tension was applied, the points *B* moved further out of the plane to produce a cube.

A cylindrical microstructure (Figure 5C) resulted from μCP with a stamp bearing the design shown in Figure 5B, etching, electroplating, and finally dissolving the capillary in aqueous HF solution. Figure 5D shows the microstructure after axial deformation. This transformation converts

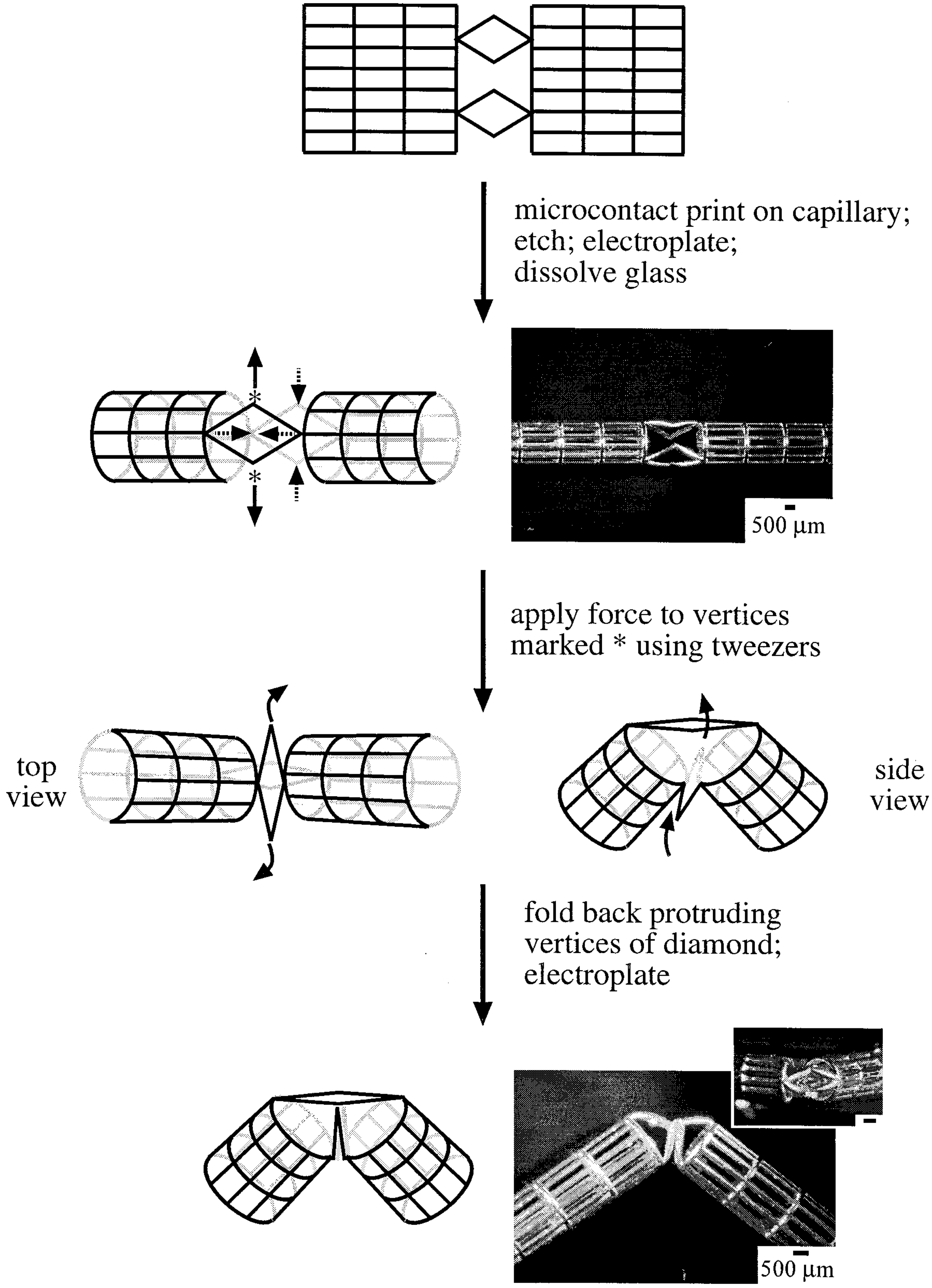

Figure 4. Free-standing cylindrical microstructures can be deformed to produce noncylindrical structures. We formed the structures shown here by μCP on silver-coated glass capillaries (~2 mm diameter), followed by wet-chemical etching to remove the silver that remained underivatized after printing, electroplating to increase the rigidity of the structure, and finally dissolution of the glass to produce a free-standing structure. (A) Design of the stamp used for microcontact printing. (B) Schematic illustration and photograph of cylindrical microstructure with a hinge that is designed to bend. Solid arrows indicate the force applied to the structure (at the points marked *) to bend it. Dashed arrows indicate the resulting motion of the structure. (C) Schematic illustration of the bent microstructure and the forces applied to it to bend the protruding points back and solidify the structure. (D) Microstructure, shown in part B, after bending and further electroplating to strengthen the structure.

the patterned cylinder with D_{4h} symmetry into a 3D microstructure with O_h symmetry (if only the cube, independent of the remaining structure, is considered; otherwise, it remains D_{4h}).

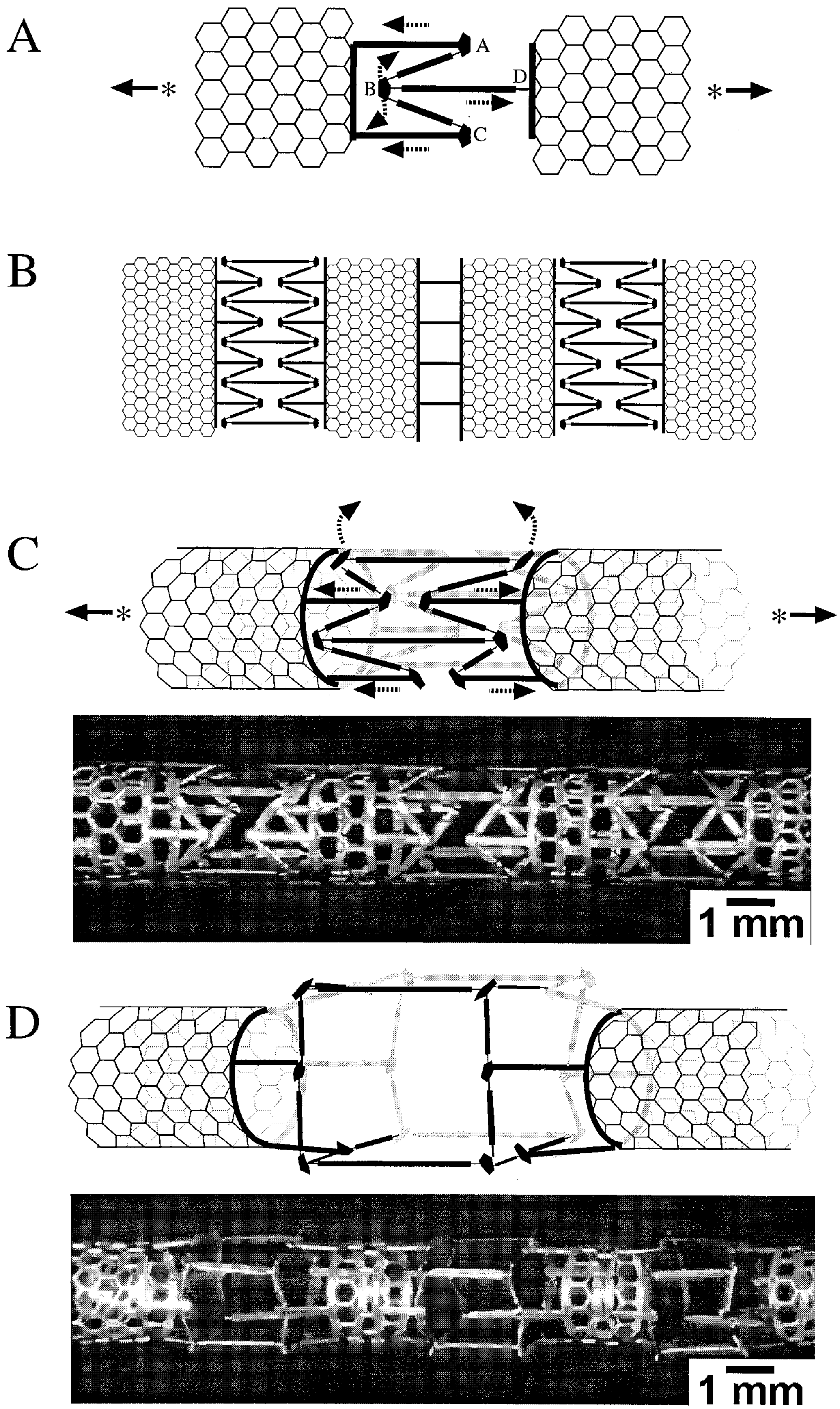

Figure 5. Cylindrical microstructures can be transformed into noncylindrical structures by the application of an axial deformation. (A) Design for 2D pattern that deforms under tension. Designs for and optical micrographs of a 2D pattern (B) designed to be projected onto a cylindrical substrate (C) by μCP, electroplated to increase its rigidity, released from the support, and deformed under tension to produce a 3D structure with noncylindrical symmetry (D).[23]

Possible structures are not limited to the design shown here. When the relative dimensions and angles of the wires that form the cube are varied, the size of the cube will vary or a cuboid will result. The pattern need not be 4-fold symmetric: any number of repeat patterns around the circumference of the capillary is possible, and each pattern need not be identical nor itself symmetrical.

In the case of both of the deformable cylindrical structures shown here (Figures 4 and 5), it would be useful to measure the forces required to cause the deformations. Although the dimensions of the microstructures make this type of characterization difficult, we are attempting to develop appropriate techniques to do so.

Electrochemistry as a Micron-Scale Tool for Welding: Fabrication of Three-Dimensional Microstructures with Complex Topologies. In addition to giving structural rigidity to fabricated structures and allowing the deformation of appropriate microstructures, electrochemistry is an invaluable tool for joining or welding at the micron scale. As Figure 3A illustrates, when two or more electrically conductive structures are held in close proximity during electroplating, the structures come into contact and weld as the metal deposit thickens. We have taken advantage of this ability to join discrete structures on different substrates into a topography that is not accessible using a single substrate.

One of the simplest structures with a complex topography is a linked chain with freely moving components. In a planar geometry, using standard techniques (photolithography and through-mask electroplating), the fabrication of this structure is impossible in a single layer and difficult with multiple layers.[42] Topologically, two intersecting planes are more complex than a single plane and allow the fabrication of a chain (Figure 6A): if every second link, for example, is projected onto one plane and all other links are projected onto the second plane so that each link crosses the line defined by the intersection of two planes, then if the planes can be removed, a linked chain results. The line defined by the edges of two cubes or rods in close contact, or the tangent line formed by two adjacent cylinders is topologically equivalent to the intersection of two planes—all define a line around which to perform fabrication (Figure 6A). We used nonplanar, through-mask electroplating, using a flexible mask (Figure 2) to pattern a pair of capillaries. After plating a thin layer of metal into the molds, we brought the capillaries into close proximity and aligned them. Electroplating welded the discrete structure into a linked chain (Figure 6A).

This methodology for the fabrication of intertwined structures can be extended to more complex structures. If the structure consists of a single knotted loop (e.g. a trefoil knot) rather than being composed of individual links, it can be fabricated by microcontact printing the pattern because the structure, once it begins to electroplate and becomes welded, is no longer composed of discrete, electrically isolated pieces—it is one continuous loop. Figure 6B shows an image of a microfabricated trefoil knot and the designs used to produce it. The two distinct patterns shown were required to produce the knot. Thin, temporary connecting wires (see diagram) ensured all sections of the pattern would electroplate immediately. After forming these patterns in metal by printing and etching on two different capillaries, we aligned the patterns to one another, made electrical connection to them, and electrochemically welded them together. The trefoil knot resulted on dissolution of the glass capillaries and removal of the connecting wires using a pair of microscissors. We believe that this methodology should make it possible to produce a knot of arbitrary complexity with just two cylinders.

The manual alignment step required for both the chain and the trefoil places a lower limit on the size of capillary that can be used in this type of 3D microfabrication and limits the minimum feature sizes; we are currently exploring alternative methods for assembly.

Conclusions

Microfabrication of metallic 3D structures and 3D structures with complex topographies is a challenge that we can now begin to meet. We have combined two techniques—soft lithography and microelectrochemistry—that together can generate metallic, 3D microstructures. Soft lithography is a convenient method of planar pattern transfer and is the only practical method that we know for parallel pattern transfer to nonplanar substrates. By electroplating ductile metals, we have been able to use controlled distortions of originally planar patterns to convert (i) planar microstructures into 3D structures, (ii) cylindrical structures with hinges into bent structures, and (iii) cylindrical structures into structures with non-cylindrical symmetry. By electrowelding, we have been able to join discrete structures on different substrates so that the resulting structure has a complex topology.

We chose to work with structures having feature sizes > 25 μm. At this scale, rapid prototyping is a useful, inexpensive technique for the production of photomasks and stamps. Features of this size, when combined with structural features of 100 μm size, concentrate stress and allow the controlled deformations and alignment steps needed for 3D fabrication to be carried out relatively easily. Reduction to smaller scales will require the development of alternative strategies for assembly and alignment of components and for the controlled deformation of 2D precursors into 3D structures.

Experimental Section

Fabrication of Flexible Masks for Photolithography and Stamps for Printing. For features smaller than ~25 μm, we used a standard chrome mask for photolithography. For features larger than 25 μm, and for directly patterning nonplanar substrates, a rapid prototyping technique described previously[27] generated masks for photolithography. In this method, we designed a pattern using a CAD program (Macromedia Freehand 7.0). Designs were printed onto transparencies using a commercial laser-assisted image-setting system (Herkules PRO, 3386 dpi, Linotype-Hell Company, Hauppauge, NY). Using the flexible transparencies as photomasks or a chrome mask, we performed photolithography either on silicon wafers (Silicon Sense, Nashua, NH) to produce the masters for producing "stamps" or on cylinder structures to form molds for electroplating.

Surface treatment of the silicon wafer by exposure to the vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technology, Bristol, PA) in a vacuum desiccator prevented adhesion of the elastomer to the wafer during the curing step. Elastomeric stamps for microcontact printing (μCP) were formed by casting poly(dimethylsiloxane) (PDMS) prepolymer (Sylgard 184, Dow Corning, Midland, MI) against a master.[23] After curing at 65 °C for ~2 h, we removed the stamp from the master.

Preparation of Planar Substrates. We cleaned glass microscope slides (VWR Scientific, Inc., Media, PA) by immersing them in a piranha solution (concentrated H_2SO_4/30% H_2O_2 (3:1)—*Caution: piranha solution can react violently with organics and should be handled with care*) and then rinsed them with large quantities of distilled water and absolute ethanol. The slides were finally blown dry in a stream of filtered nitrogen. Using an electron-beam evaporator, we coated them with titanium (50 Å; adhesion promoter) and then silver (500 Å).

Preparation of Cylindrical Substrates. Glass capillaries (Pyrex, diameter ~ 1.7 mm) served as cylindrical substrates. We

(42) Ikuta, K.; Maruo, S.; Kojima, S. *Proceedings MEMS'98. Eleventh Annual Workshop on Micro Electro Mechanical Systems*; IEEE: New York, 1998; pp 290–5.

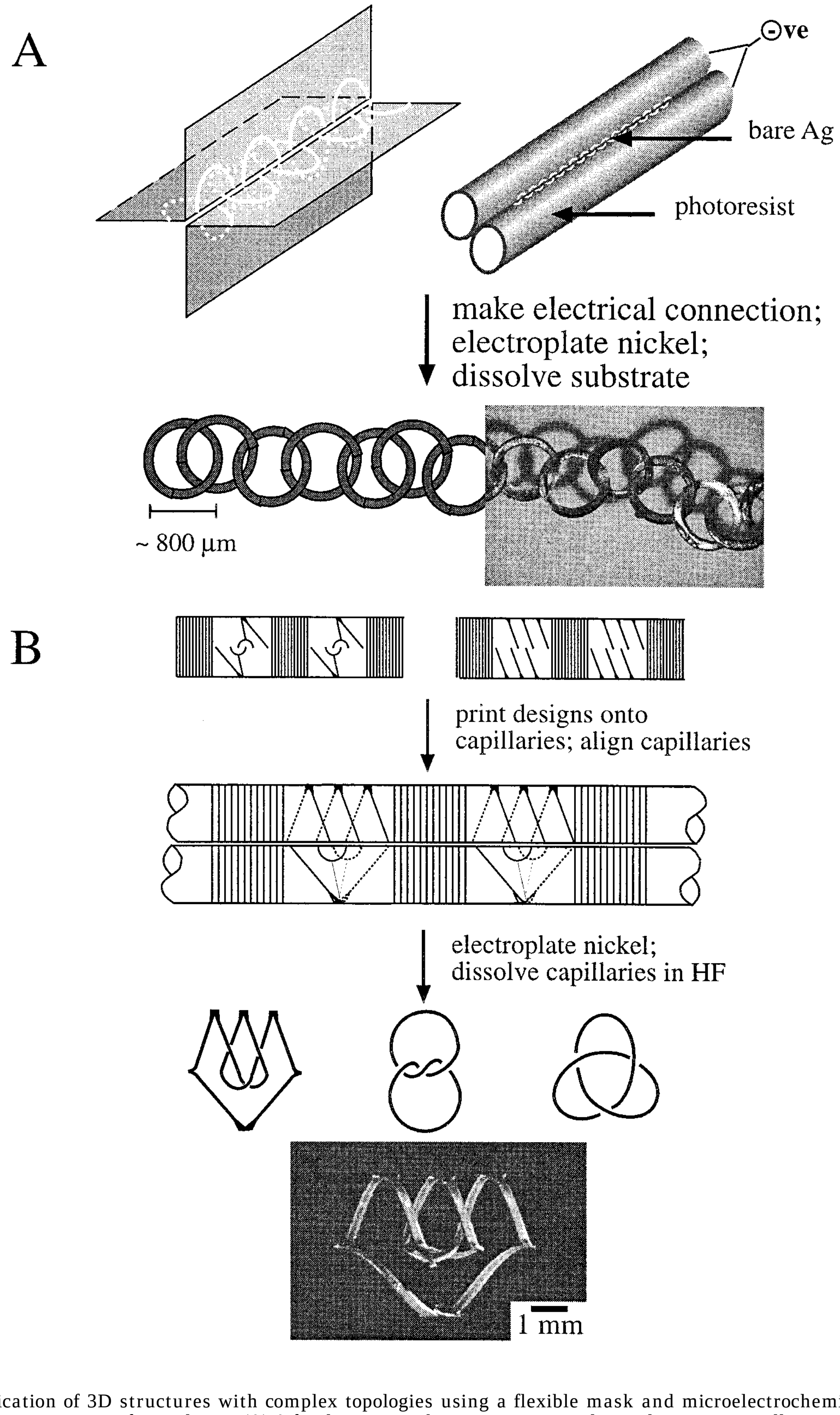

Figure 6. Fabrication of 3D structures with complex topologies using a flexible mask and microelectrochemistry. Performing fabrication at the intersection of two planes. (A) A freely moving chain. We patterned two glass microcapillaries, coated with a 500 Å film of silver, using a flexible mask, as shown in Figure 2. The white regions on the capillary represent regions of exposed metal, and the gray regions represent regions coated with photoresist. After aligning the two capillaries under a microscope so that their patterns were brought into register, we glued them in place, made electrical connection to them remotely, and plated metal onto their exposed regions. This plating also welded the structure together. We then dissolved the capillaries in aqueous HF and released a freely jointed, interlinked chain.[23] (B) A trefoil knot. We microcontact printed the two designs illustrated onto two silver-coated glass microcapillaries. After etching the unprotected silver and titanium, we aligned the two capillaries under a microscope so that their patterns were brought into register (see image), and we glued them in place, made electrical connection to them, and electroplated nickel. During the plating step, the patterns became welded together. We then removed the extra connecting wires with a pair of microscissors and dissolved the capillaries in aqueous HF.

prepared them by cleaning them in piranha solution. Using an electron-beam evaporator, we typically coated these substrates with titanium (25 Å, as an adhesion promoter), followed by silver (500 Å). Mounting the samples on a stage that rotated about two orthogonal axes during the evaporation allowed metal to be deposited all around the substrates in a single evaporation.[38]

Microcontact Printing (μCP) on Planar and Cylindrical Substrates. An elastomeric stamp, having micron scale relief, transferred an "ink" to a substrate during microcontact printing. This ink either protected the underlying surface against etching or initiated deposition of material. Typically, we printed a protective self-assembled monolayer (SAM) of hexadecanethiol onto silver-coated substrates. For the cylindrical substrates, we used a laser-aligned arrangement of precision translation and rotation stages[37] to control the relative orientation of the stamp and substrate, the pressure applied during printing, and the rate of printing. For the planar substrates, we simply placed the inked stamp in conformal contact with the substrate for about 10 s. After printing, immersion of the substrates in an aqueous ferri/ferrocyanide bath (1 mM $K_4Fe(CN)_6$, 10 mM $K_3Fe(CN)_6$, 0.1 M $Na_2S_2O_3$) for 20 s removed the underivatized silver. Exposure of the substrate to aqueous 1% HF for ∼15 s etched the titanium uncovered by removal of the layer of silver and left an electrically isolated microstructure on the substrate.

Electroplating to Produce Free-Standing Microstructures. To increase the structural stability of the microstructures, we made electrical connection using silver paint and electroplated silver using a commercially available electroplating bath (Techni-Silver E2, Technic Inc., Providence, RI) at a current density of 20 mA/cm^2 for ∼15 min using the thin layer of silver as a template for deposition. Once the structure was ∼20 μm thick, we removed the glass support by placing it in concentrated aqueous HF (49%) for ∼30 min (Caution: the direct exposure of skin to concentrated HF can result in damage to skin and bones).

Application of Deformations to Produce 3D Microstructures. (a) From Planar Substrate by Folding. We folded the structure using a pair of tweezers. After placing the series of tabs into the set of slots, we electroplated the structure further (∼30 μm thick) to weld it together.

(b) From Planar Substrate by Out-of-Plane Deformations. We deformed each component of the array to produce the square-based pyramid by moving the center of the structure out of the plane using a pair of tweezers. Further electroplating (∼10 μm of additional silver) made the structure more rigid.

(c) From Cylindrical Substrate by Bending at Joints. We bent the diamond-shaped joint using a pair of tweezers: on pushing the two vertexes, not directly connected to the rigid regions of the cylinder (marked *), out relative to the axis of the cylinder, the other two vertexes, and the rigid sections of the mesh to which they were attached, began to move toward one another. The diamond on the outside of the joint then became deformed slightly in the opposite sense. We bent the protruding vertexes of the diamond on the inside of the joint back toward the other diamond and electroplated the joint further (∼30 μm thicker) to fix it rigidly in place.

(d) From Cylindrical Substrates by Applying an Axial Deformation. Tension applied to a structure by pulling on its opposite ends with tweezers caused the metallic structure to "pop" into its final form. We had placed drops of epoxy at both ends of the capillary to prevent it from being crushed by the tweezers. Further electroplating (see above) after this transformation reinforced the structure and made it rigid.

Photolithography on Nonplanar Substrates. Substrates (usually metal-coated) were coated with photoresist by using a syringe pump (Harvard Apparatus, Harvard, MA) to pull them slowly (1 cm/min) from solution (Shipley 1813, Microlithography Chemical Corporation, Newton, MA). Placing the substrates on a hot plate at 105 °C for 3.5 min hardbaked the photoresist. After wrapping a flexible mask (produced by rapid prototyping) around the substrate, we exposed the photoresist to UV light for ∼8 s using a Karl Suss mask aligner. The pattern developed on immersion of the substrate in Shipley Developer 351.

Electrochemical Welding of Structures on Two Capillaries to Produce Topologically Complex 3D Microstructures. Under an optical microscope, we aligned substrates patterned by photolithography so that they were in close proximity to one another and their patterns matched. After making electrical connections to the metal, electroplating nickel, from a nickel sulfamate-based plating bath (Techni-Nickel "S", Technic Inc., Providence, RI) held at 45 °C for ∼30 min at a current density of ∼20 mA/cm^2, into areas defined by the photoresist, electrochemically welded together the patterns on the substrates. We released the welded structure from the substrates by dissolving the photoresist in acetone, the silver in an aqueous ferricyanide bath, and the titanium and glass in concentrated aqueous HF solution.

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