# Fabrication of Topologically Complex Three-Dimensional Microstructures: Metallic Microknots

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**Abstract:** This paper describes a method for fabricating three-dimensional (3D) microstructures with complex topologies—trefoil, figure eight, and cinquefoil knots, a chain with complex links, Borromean rings, a Möbius strip, and a torus. This method is based on the strategy of decomposing these structures into figures that can be printed on the surfaces of cylinders and planes that contact one another. *Any* knot can be considered as a pattern of crossings of lines, in which one line crosses "over" or "under" the second. We map these "over" and "under" crossings onto the surface of a cylinder and show that only two cylinders, in tangential contact (with axes parallel) and with lines allowed to cross from the surface of one to the surface of the second, are required to make any knot (or, in a combinatorial mathematical sense, any graph) in a topography that consists only of smooth curves. To form free-standing metal microstructures, we begin by printing appropriate patterns onto a continuous metal film on two cylinders using microcontact printing: these patterns are developed into patterns of exposed metal by etching or by covering with polymer. The cylinders are aligned (using a new procedure) with a slight separation between them. The metallic patterns on them are used as cathodes for electrodeposition, which strengthens the metal features and also welds them into a continuous structure. When electrodeposition and welding are complete, the cylindrical templates are dissolved, and the topologically complex, 3D, free-standing metallic structures are released.

## Introduction

Photolithography has been the dominant technology used to make microstructures. It is an extraordinarily versatile methodology for preparing planar systems but is much more limited in its application to three-dimensional (3D) structures (especially structures involving curved surfaces). The most common method of using photolithography to make 3D structures involves stacking multiple, registered layers.[1] This method can form topologically complex 3D microstructures but cannot form smooth, 3D curves or sheets. As alternatives to conventional photolithography, stereolithography,[2,3] laser writing,[4−7] and projection photolithography using systems of mirrors[8] have been explored for fabricating 3D structures; all have limitations. Micromachining,[9−11] although it can be used to make 3D structures, is also limited in the materials it can accept and the structures it can generate.

It is probable that there is no single technology for microfabrication in 3D that has the generality of conventional projection photolithography for microfabrication in 2D. Instead, a number of more specialized techniques are being developed for specific purposes.[12] We have developed a set of nonphotolithographic techniques for microfabrication that are based on the printing of self-assembled monolayers (SAMs) and the molding of organic polymers;[13] we call this set of techniques collectively "soft lithography" because it uses an elastomeric (i.e., "soft") polymeric structure as the pattern transfer agent. Soft lithography provides methods of fabricating a number of types of structures that cannot be prepared conveniently by photolithography: for example, structures involving 3D, curved surfaces,[14,15] biologically relevant and fragile materials,[16] and structures incorporating materials not compatible with photolithography for other reasons.[13] It is especially useful for rapidly and inexpensively prototyping[17] structures with feature sizes $\geq 20\ \mu m$.

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Here, we take advantage of the ability of soft lithography to print patterns on curved surfaces (in this case, cylinders).[14] We make 3D structures composed of smooth curved sections using a three-step process: (1) we pattern two cylindrical substrates with appropriate metal structures using a combination of microcontact printing ($\mu$CP) and electrodeposition; (2) we join these structures (in this same electrodeposition step) by electrowelding; and (3) we separate the metal structures from the supporting cylinders (usually by dissolving the cylinders).

This paper demonstrates strategies for making topologically complex, small objects by producing structures—knots (including linked knots), a torus, a Möbius strip—that would be difficult or impossible to fabricate using photolithography. These microstructures are not intended to be useful; rather, they are intended to explore the feasibility of making microstructures composed of complex curved surfaces, or having topologically and topographically complex connectivity. We have chosen to fabricate these structures using metal both because, in that form, they are strong enough to survive manipulation and characterization as free-standing entities, and because electrodeposition provides a method of joining microscale patterns on different cylindrical surfaces. Modifications of these structures may also be useful in generating magnetic fields with unusual geometries in small regions of space.

The key element in the strategy is the process comprising decomposition of objects with complex topologies into separate subpatterns, the printing of these subpatterns onto the surface of different cylinders, and the recombination of these subpatterns to generate the desired topology. Patterning on cylinders solves two central problems—allowing lines to cross without touching, and controlling the topology of tapes—that are relevant to fabricating topologically complex 3D microstructures.

**The Topology of Crossing Lines.** We analyze the topology of a 3D structure of intertwined lines by first projecting it onto a plane. The 3D structure could be either a knot (a closed, 3D, nonintersecting curved line), a set of links (multiple closed curved lines that cannot be separated by deformation), or a graph (a set of vertices, together with a set of edges pairing some of the vertices).[18−20] We permit the structure to be deformed, as though made of elastic, before projection so that the resulting pattern on the plane can be decomposed into a series of segments of curved lines, and a set of points at which these segments cross. At crossing points, one line goes “over” and one line “under”. One can always deform the object so that in the planar diagram no more than two lines cross at a point. The ability to fabricate arbitrary patterns of “over” and “under” crossings thus makes it possible to fabricate any of these kinds of structures; our method, which is described in detail later, is, in principle, entirely general and is applicable to all knots, links, and graphs.

Figure 1 shows the result of applying our method to a trefoil knot. A trefoil knot (and its mirror image) has a diagram with three crossings, as shown in Figure 1a. It is possible to fabricate this type of structure with photolithography by stacking multiple layers and connecting them with vias using registered, planar projections. The resulting structures, although having the desired topology, would consist of a series of right angle turns, as shown in Figure 1b. By contrast, patterning on the surface of cylinders provides a way to pass two curved segments of wires across one another, without contact, using only continuous, smooth curves (Figure 1c). All the crossings are mapped on cylinders; their “over” and “under” lines are positioned such that they do not touch each other. If only two cylinders are used to construct a knot, any curve on either cylinder must start and end on the contact line of the two cylinders when their axes are parallel and their surfaces are in tangential contact. Figure 1d shows three possible ways to achieve the “under” and “over” lines of a crossing on a cylinder: in the first figure, both lines wind all the way around the cylinder; in the second, neither line wraps around the cylinder; in the third, only one of the two lines wraps around the cylinder. In each figure, one line “crosses” the other line, even though they are not in contact, in the sense that points $p$,$r$,$q$,$s$ alternate along the contact line $L$.

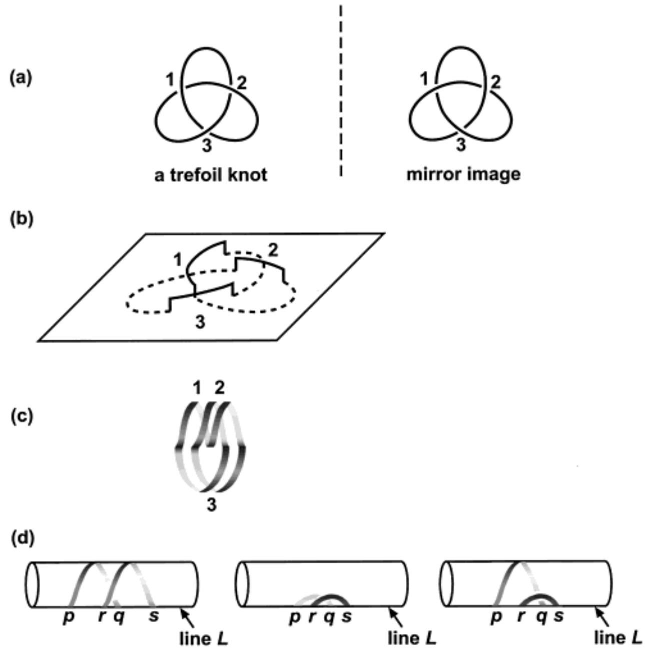


**Figure 1.** (a) Planar diagram of a trefoil knot and its mirror image, both having three crossings. (b) The trefoil knot that would be formed by stacking layers using photolithography; the patterns on different layers are connected by vertical lines and right angle turns. (c) The trefoil knot that would be formed by joining patterns on separate cylinders; the structure is made entirely of smooth curves. (d) Scheme describing the three relative positions of the “over” and “under” lines of a crossing on a cylinder. In the first figure, both lines wind all the way around the cylinder; in the second, neither line wraps all the way around the cylinder; in the third, only one of them wraps around the cylinder.

**The Topology of Tapes.** The second topological problem solved by patterning on cylinders is that of controlling the topology of tapes. A simple tape—for example, a band around a cylinder—has two sides and two edges. A Möbius strip, however, has just one side and one edge (Figure 2a). To make a Möbius strip, one can take an actual tape, twist it a half-turn, and connect the head and the tail of the tape; this type of physical manipulation is difficult or impractical when fabricating microstructures. The combination of a cylindrical pattern and a planar pattern is, however, a convenient way to make twists in a tape and, thus, to make a Möbius strip. Figure 2b shows two closed tapes with no twists: one follows the surface of a cylinder and one is flattened, bent around, and joined, all within a plane.


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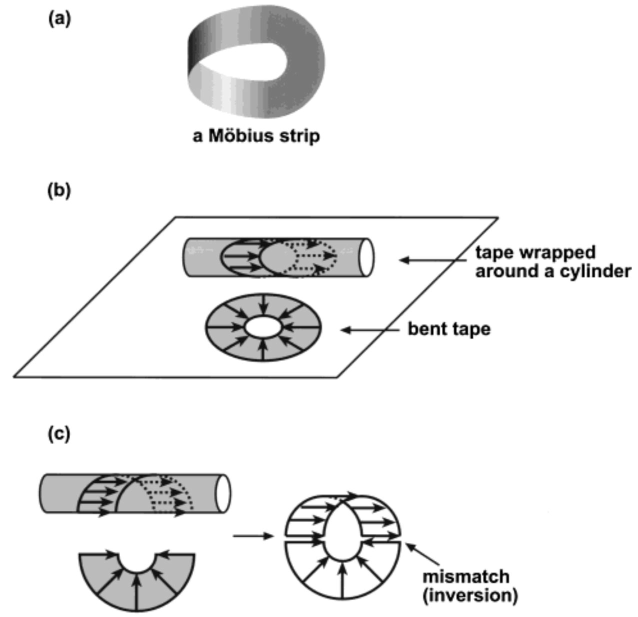


**Figure 2.** (a) A Möbius strip. (b) Schematic illustration of the difference between a strip around a capillary and a strip on a plane. An arrow does not change its direction along the strip around a capillary, which is always along the axis of the capillary, and it does when it moves along the strip on a plane. (c) When joined end to end, the two tapes form a Möbius strip.

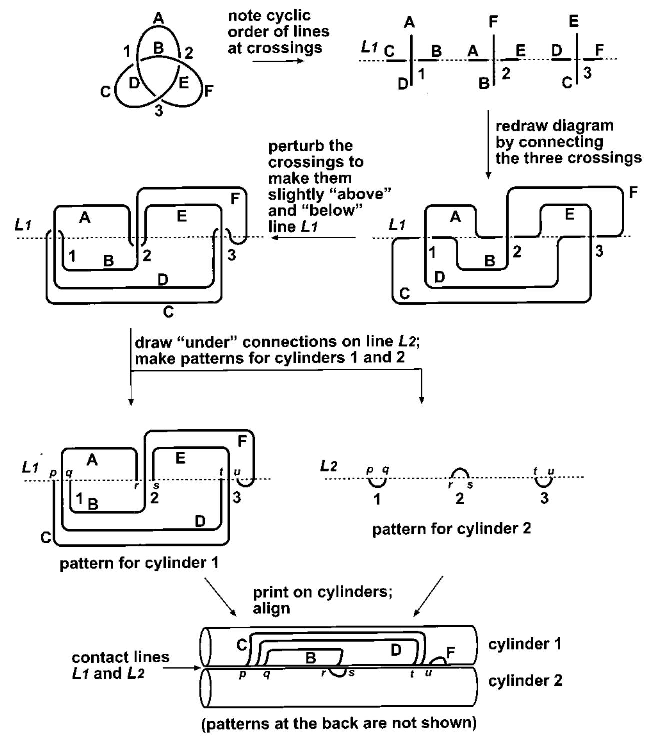


**Figure 3.** Illustration of the algorithm used to decompose a knot into paired patterns that are transferred onto two cylindrical surfaces. This illustration is based on a trefoil knot but applies to any knot. Five steps are followed: (1) labeling the crossings; (2) redrawing the crossings on a line; (3) connecting the corresponding lines of the crossings; (4) perturbing the crossings to make them slightly "above" or "below" line $L_1$; (5) making patterns for cylinders 1 and 2. Lines $L_1$ and $L_2$ can be any horizontal lines on a plane; they represent the contact lines of the two patterned cylinders when they are aligned to form the desired structure. The detailed procedure is given in the text.

In both cases, arrows drawn from an arbitrary starting point do not change their direction when they come back around to the starting point. We can cut the cylindrical tape in half by slicing lengthwise down the cylinder. If we perturb the tape by displacing its ends slightly, the ends will match the ends of a half of the planar tape, as depicted in Figure 2c. Connecting the ends gives a closed tape with a half-twist—a Möbius strip.

## Topological Analysis

Now we show the ability to accommodate crossings—and thus to make any knot, set of links, or graph—by patterning on cylinders. To make the experimental realization of these knots as simple as possible, we wish to use as few cylinders as possible for a given structure. Here, we show, by decomposing a knot in steps that are general for any knot, set of links, or graph, that two cylinders suffice for its fabrication.

We wish to convert a 2D diagram of any knot into two patterns that we will print on two cylinders. We illustrate the steps of our general method, using the trefoil knot as an example. The crossing number of the trefoil knot is three,[21−23] as shown in Figure 3 (top left). Because crossings are formed in parallel by our method of fabrication, additional crossings do not increase the difficulty of fabrication. The procedure requires five operations:

(1) Number the three crossings of the trefoil knot 1, 2, and 3 and label the six connecting lines between crossings A, B, C, D, E, and F (Figure 3, top left).

(2) Draw the three crossings on a horizontal line $L_1$ with the "under" lines horizontal. Label the four lines that emerge from each crossing in the same cyclic order in which they occur in the original trefoil knot. Each crossing can be drawn in two ways which differ by 180° rotation, but which have the same cyclic order of lines. Any permutation of the order of the crossings on line $L_1$, and either rotation of the crossing, will give a topologically equivalent diagram, but some permutations and rotations lead to simpler patterns than others.

(3) Redraw the diagram by connecting corresponding lines having the same label (A to A, B to B, etc.) with nonintersecting lines.

(4) Perturb the crossings so that the crossings sit slightly "above" or "below" the line $L_1$. The purpose of this step is to ensure that the final structure is composed of smooth curves, without cusps.

(5) Separate the "under" connections (the short arcs in the second figure in the left column) from the rest of the diagram and draw them along a new line $L_2$; this pattern is the one printed on cylinder 2. The rest of the pattern remaining after the "under" connections are removed is the pattern that is printed on cylinder 1. The contact points on lines $L_1$ and $L_2$ are labeled with letters p, q, r, s, t, and u; points to be matched are labeled with the same letter. Our convention for drawing patterns in the figures is to imagine that a pattern is raised and inked on a cylinder and that it is rolled on the plane to give the flat pattern. Alternatively, we imagine rolling a cylinder over a raised and inked flat pattern to determine the corresponding pattern on the cylinder. For example, in Figure 3, we draw patterns on cylinders 1 and 2 by imagining rolling the cylinder over the corresponding flat patterns. Bringing the cylinders into tangential contact along lines $L_1$ and $L_2$ and aligning the contact points constructs an object with the desired topology—a trefoil knot.

(21) The crossing number of a knot is the minimum number of crossings that the knot can have in a 2D projection (cf. ref 22).

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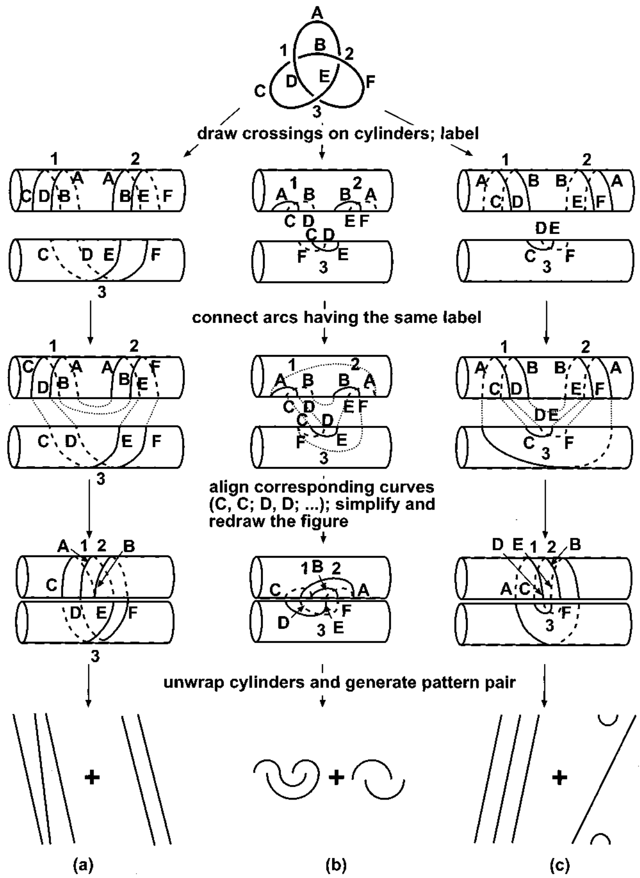


**Figure 4.** Three ways to form patterns that are used to generate trefoil knots. (a) Both "over" and "under" lines of all crossings wind all the way around the cylinders. (b) Neither the "over" nor the "under" line of any crossing winds all the way around the cylinders. (c) Lines of some of the crossings wind all the way around the cylinders. Note that the thin dotted lines are imaginary lines included simply to indicate connectivity.

In general, our procedure generates two patterns having 2$n$ connections between them for a knot whose chosen planar diagram has $n$ crossings.

## Decomposition of Knots into Pairs of Two-Dimensional Patterns

Any knot can be decomposed into many different pairs of flat patterns: some yield smoother structures than others. In Figure 4, again using the trefoil knot as an example, we show three different pairs of planar patterns for this knot, generated by using three methods for mapping crossings of a knot onto only two cylinders (Figure 1d). The pattern shown in Figure 4a is generated by wrapping both "over" and "under" lines of each crossing around the cylinders; in Figure 4b, neither the "over" nor the "under" line of any crossing wraps around a cylinder; we combined the two methods to form the pair of patterns shown in Figure 4c. These three approaches give different pairs of patterns and lead to different spatial arrangements in the final microstructures; they follow, however, a similar procedure, starting from the diagram of the trefoil knot:

(1) Label all crossings and connecting lines as in Figure 3, top left.

(2) Draw each crossing on either of two parallel cylinders using the methods for mapping crossings shown in Figure 1d. Label each crossing, and the four lines emerging from that crossing, so that they retain the same cyclic order and the same "under" or "over" orientation as in the starting diagram of the trefoil knot. Note that the trefoil knot is a chiral object, so the topology of the original figure must be retained.

(3) Connect any pair of lines having the same label with imaginary lines (shown as thin dotted lines in Figure 4) without introducing additional crossings.

(4) Simplify the figure by shortening the imaginary lines and by rotating the four lines of a crossing where desired. During the simplification, do not generate new crossings. Once the simplification is finished, what remains of the imaginary connecting lines is added into the patterns. (In the center figure on the left in Figure 4, an entire wrapping around the cylinder has been removed from A, allowing the imaginary, dotted portion of B to shrink to a point.)

(5) Observe how the patterns from the cylinders would roll onto 2D planes to determine the flat patterns required to make the photomasks for photolithography.

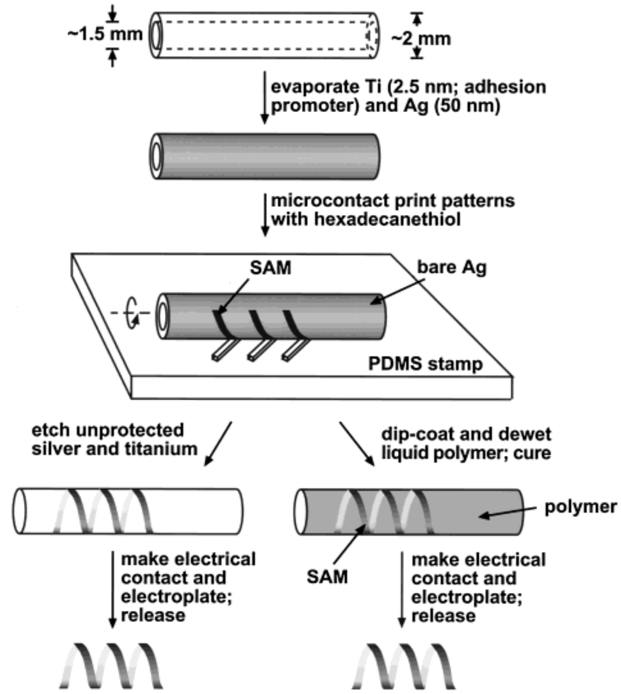


**Figure 5.** Outline of the use of microcontact printing to pattern cylindrical surfaces. Glass capillaries (~2 mm diameter) were coated with titanium (as an adhesion promoter), followed by silver or gold (Ti/Ag = 2.5 nm/50 nm for wet-chemical etching; Ti/Au = 1 nm/10 nm to control polymer wetting) by electron beam evaporation. Microcontact printing of hexadecanethiol using an elastomeric stamp transferred the patterns from the stamp to the glass capillaries. We used the hexadecanethiolate SAMs in two ways. First, they served as resists for wet-chemical etching. If the pattern remaining after etching was electrically continuous, we simply made electrical connection to the pattern and used it as the cathode in electrodeposition of metal. After electrodeposition, the microstructure was released by dissolving the cylindrical substrate. Second, the SAMs acted as templates, preventing the deposition of a hydrophilic liquid epoxy prepolymer (SU-8 2); when the printed capillary was dipped into and pulled out slowly from the liquid prepolymer, the prepolymer covered all of the surface except the pattern. We used the "exposed" metal layer (covered only by SAMs) as a cathode, made electrical contact, and electroplated to form the microstructure. We released the structure by dissolving the polymer and the cylindrical substrate. Even though the pattern was discontinuous, the entire pattern could be electroplated because the underlying metal layer acted as a conductive sheet.

## Results and Discussion

**Methods of Fabrication. (a) Microcontact Printing ($\mu$CP)**

**on Cylindrical Surfaces.** Microcontact printing provides an experimentally simple method of transferring 2D, 100-$\mu$m-sized patterns onto cylindrical surfaces (Figure 5). In the experiments described here, we used hexadecanethiol (HDT) to form the patterned SAM on a cylinder (~2 mm in diameter) covered with a thin layer of silver or gold. We use this patterned SAM in two ways: (1) as a resist against etching—after wet-chemical etching to remove the un-derivatized metal, the metal pattern left on the substrate can serve as the cathode for electrochemical deposition of metal; (2) to control the wettability of the surface and to direct liquid to specific regions—after dip-coating, dewetting liquid prepolymer leaves the *unprinted* metal covered. After curing of the polymer, electrodeposition takes place only on the metal pattern covered with SAM.

**(b) Electrodeposition and Welding.** We used electrochemistry to generate mechanically strong structures and to join (or weld) metal structures together. When two or more electrically conductive structures are used as cathodes during electroplating, metal grows on each. If the structures are positioned close together, and if a metal feature on one cylinder aligns with a metal feature on the second, these features come into contact and weld together as the metal grows by electrodeposition. Using this procedure, discrete patterns on different substrates can be joined to generate a more complex structure.

Since many metals and conductive polymers can be deposited electrochemically, electrochemistry could be used to fabricate complex 3D microstructures in a variety of materials. During electroplating, the growth of metal is approximately isotropic and results in structures with rounded side walls.

**(c) Electroplating Discontinuous Patterns.** After microcontact printing and etching, we electrodeposited metal on the remaining patterns to grow, weld, and strengthen structures. If the patterns on the cylinders are conducting and electrically continuous after printing and etching, it is straightforward to use electrodeposition to grow the structures and weld structures on different substrates. For many patterns, the elements on which electrodeposition is to occur are electrically discontinuous; electroplating obviously does not occur on electrically isolated structures. We examined two strategies to generate cathodic structures that would allow continuous electroplating.

(1) *Adding thin, sacrificial lines.* In one, we included thin correcting wires in the printed pattern. This process is simple and applicable to any pattern, but, to form the desired structure, these sacrificial components—which also are thickened during electroplating—must be removed *after* the electrodeposition. The removal step of the sacrificial components leaves marks and stubs on the final structure.

(2) *Dip-coating and dewetting prepolymer.* In the other, we again printed the desired pattern but used the hydrophobic SAM—not to prevent etching, but to prevent the deposition of hydrophilic liquid prepolymer when the cylinder was immersed and withdrawn slowly from the prepolymer. The area of patterned SAM was more hydrophobic than the "bare" metal (not covered by SAM); the liquid prepolymer spontaneously dewetted from the printed regions but covered other metal regions. The liquid prepolymer was cured into a solid; this polymer structure acted as a thick-film resist to plating. Electrodeposition occurred exclusively on the areas that had been covered only by the SAM. This method gives metal structures with smooth edges, because it obviated the manual cutting step that is used to remove the sacrificial components in the first method.[24]

**(d) Registration.** Registration is an inevitable issue in the fabrication of complex topology. Since the patterns are on separate cylinders, the connections on the contact lines cannot be easily seen from above when the two cylinders are aligned on a flat substrate. Here we describe a method facilitating the registration of patterns on cylinders (Figure 6). To present all the features to be aligned in the microscope used during registration, we started with two bare cylinders which had the same size of the cylinders bearing the features: they were placed close but not touching and side by side on a flat substrate

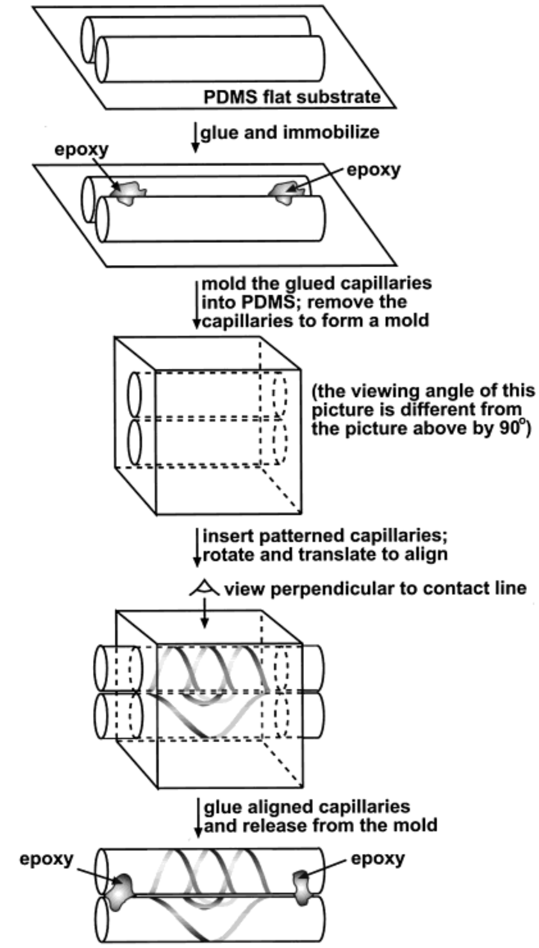


**Figure 6.** Schematic illustration of the procedure used to register patterns on separate capillaries. An alignment jig was generated by placing two silanized bare capillaries, having the same size as the capillaries to be aligned, parallel and close together (spaced by ~15 $\mu$m when manually handled) on a flat PDMS piece (glass capillaries have conformal contact with PDMS to prevent them from moving around during manipulation, and PDMS can be cut easily). We glued them together with 5-min epoxy at their ends and molded them into PDMS. After the PDMS had cured, we cut off the glued ends of the capillaries with a diamond scribe and removed the capillaries (after swelling the PDMS mold in methylene chloride for 1 h, the capillaries would slip out of the mold by themselves or by pulling with a small force) to give a PDMS mold with two cylindrical vacancies. We inserted patterned capillaries into the PDMS mold and, by viewing from a sidewall, rotated and moved the capillaries to align the patterns on them so that the patterns matched to form the desired structure. We glued them together with epoxy at their ends and released them from the PDMS aligner by cutting it away with a scalpel.

(24) The process imposes a few requirements on the prepolymer: it must be hydrophilic (the prepolymer SU-8 2 we used has a contact angle of less than 20° on the surface of bare gold and 78° on a gold surface covered with a SAM of HDT); it must polymerize easily to a solid; the solid polymer must not be electrically conductive nor soluble in the electroplating bath; the solid polymer must be removable after electrodeposition without damage to the structure.

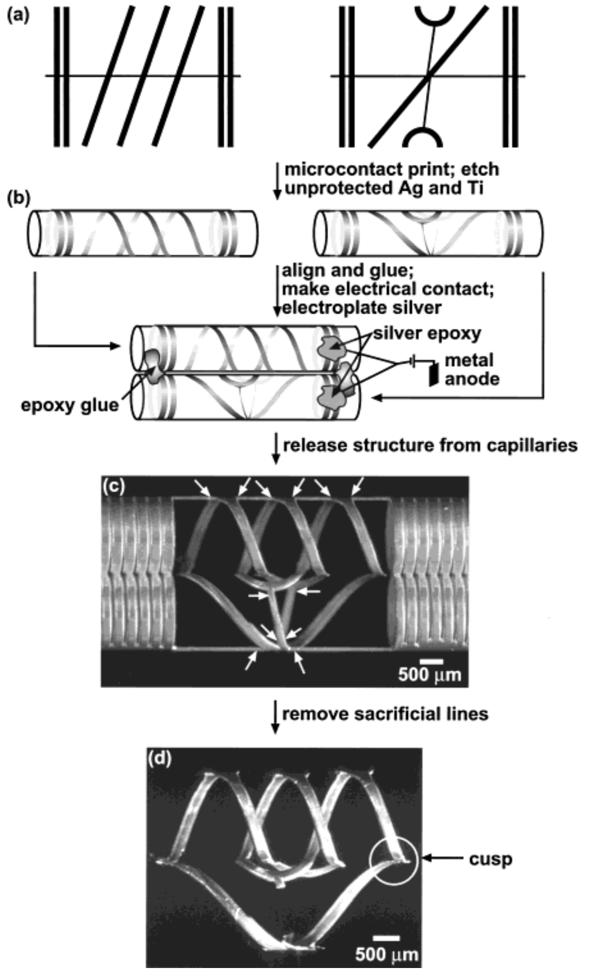


**Figure 7.** Outline of one procedure used to generate a trefoil knot. (a) The patterns were from the pattern pair generated in Figure 4c, and we included thin (30 $\mu$m) sacrificial lines together with thicker (100 $\mu$m) structural lines. The vertical lines at the ends of both patterns were not parts of the knot; they formed rings on the capillaries after microcontact printing and were included as pads to which to make electrical connections. (b) The fabrication process. After microcontact printing the two designed patterns onto two silver-coated capillaries (~2 mm), we etched away the unprotected silver and titanium. Under a stereomicroscope, we inserted the capillaries in a jig (see registration section) and aligned the patterns on them so that these patterns formed a trefoil knot. After we glued the ends of the two aligned capillaries together with epoxy and removed them from the mold, we made electrical connection by applying silver paint on the rings at the ends of capillaries. We electroplated silver (~20 mA/cm$^2$) until the patterns on the capillaries joined. In the final step, the glass capillaries were dissolved in aqueous HF solution to release the structure. (c) Optical picture of the structure released from the glass substrates. The sacrificial thin metal lines grew during electroplating. We cut the sacrificial lines (arrows indicate where the cutting happened) with a small pair of scissors to form the trefoil knot. (d) Micrograph of the trefoil knot.

(placement was manual, but they were spaced by ~15 $\mu$m) and immobilized by gluing at their ends. A transparent mold of PDMS was formed by curing PDMS prepolymer against these two glued cylinders and removing the two cylinders. When we placed two patterned cylinders to be aligned in this mold, we could both observe them and manipulate them by rotation around their axes and translation along their axes. This manipulation made it possible to match the patterns on one cylinder to that on the other, and thus to achieve the required registration. Because we view from the back of one cylinder (see Figure 6), one of the two patterned cylinders should be transparent.

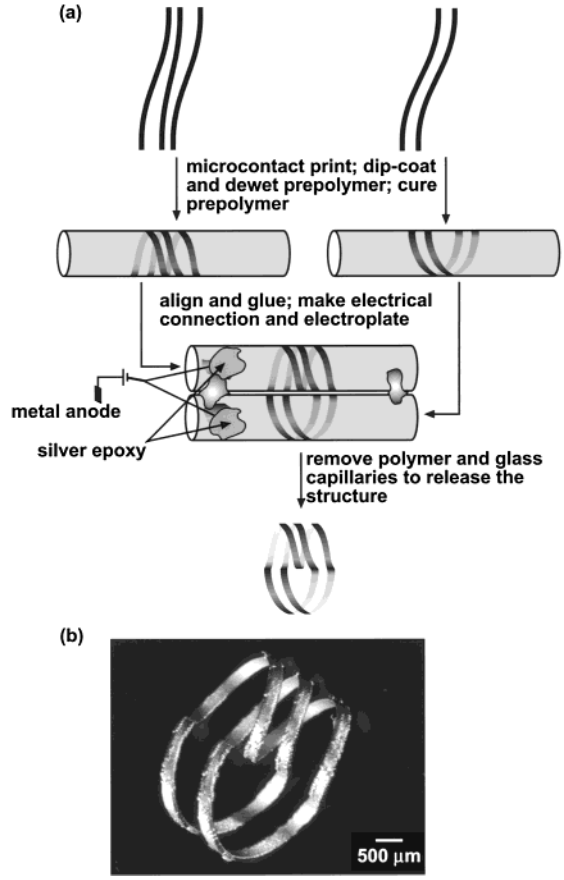


**Figure 8.** (a) Schematic illustration of the fabrication of a trefoil knot using the procedure based on dip-coating into a liquid prepolymer, and allowing dewetting to expose the pattern for electrodeposition. We started with a set of different patterns (Figure 4a) from that used in Figure 7 for a trefoil knot, which make a connection on the first cylinder during microcontact printing and need four connections between the two capillaries. The straight lines in the pattern pair shown in Figure 4a were slightly changed to appropriate curves to ensure the smoothness of the final structure at connection points. After microcontact printing the two patterns with hexadecanethiol on gold/titanium (10 nm/1 nm)-coated capillaries, we dipped the capillaries into SU-8 2 prepolymer and drew it out slowly from the liquid. The prepolymer was cured after it dewetted from printed regions; the cured polymer prevented electrodeposition on the unprinted area. After alignment and immobilization of the two capillaries, we scraped a small area of the cured prepolymer away at the ends of the substrates to expose the underlying metal and applied silver paint to this area to make electrical connections. Electroplating nickel (~30 mA/cm$^2$) welded the pattern. We finally dissolved the prepolymer and the glass substrates to release the trefoil knot. (b) Optical micrograph of the trefoil knot formed by this procedure.

**The Trefoil Knot.** The trefoil knot is the simplest of the knots to fabricate, and we have used it as a model system with which to explore methods of fabrication. Figure 7 shows the process we used to make a trefoil knot, starting from a pattern that included sacrificial lines. At some connection points between the two patterns, the final structure formed cusps along the tangent line (as indicated in Figure 7). The final step of cutting away the sacrificial lines required manual operations with a small pair of scissors. This manual intervention is undesirable: in addition to leaving unwanted tabs and scars, in many cases cutting is difficult or impossible because the features are small or the wires to be cut are inaccessible.

Using the method based on dip-coating and dewetting, we made another version of a trefoil knot shown in Figure 8. The

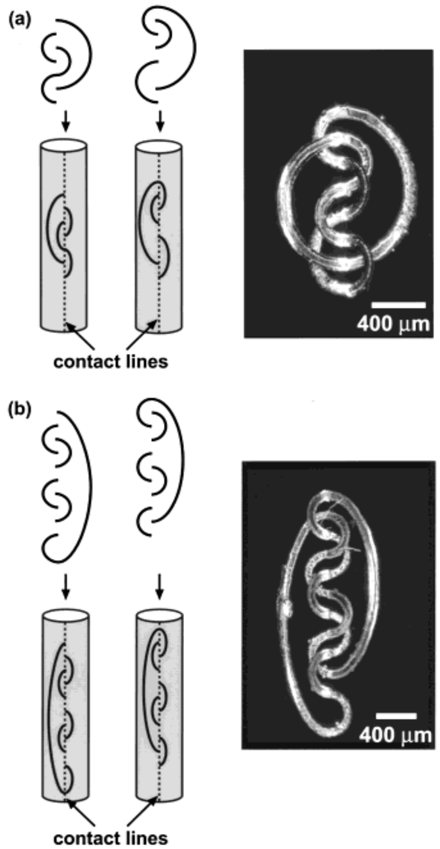


**Figure 9.** A figure eight knot and a cinquefoil knot. The pattern pair was generated by the procedure described in Figure 4b. We followed the same procedure that was used to make the trefoil knot in Figure 8. We electroplated nickel here with a current density of ~20 mA/cm$^2$. The dotted lines in the schematic show the contact lines ($L_1$, $L_2$) of two cylinders when they were aligned to form the desired structures.

ability to make two trefoils also shows that the decomposition of a topology onto two cylinders is not unique. In this pair of patterns for a trefoil knot, four connection points (in Figure 7, six connection points) between the two cylinders needed to be aligned after microcontact printing. The tangent lines at the connections of the two patterns matched each other, and the connections of the patterns were smooth after electrodeposition and welding.

**The Figure Eight Knot and the Cinquefoil Knot.** More complicated knots were also fabricated with patterning on two cylinders. Figure 9 shows the patterns for fabricating a figure eight knot (this knot has a crossing number of four) and a cinquefoil knot (this knot has a crossing number of five). This figure includes the microstructures that were fabricated. The crossing number of a figure eight knot is four, yet five crossings appear in the photograph. This apparent inconsistency is due to the fact that, in the photograph, the curve goes "under" at two consecutive crossings. These crossings could be combined by deforming the curve. The trefoil knot and the cinquefoil knot are torus knots—knots that can be embedded on a torus without crossing points. Our two-cylinder method avoids the technical complexities of patterning onto the surface of a glass torus. We note, furthermore, that our method can make *any* knot, including knots that cannot be embedded on a torus.

**A Chain of Links.** While a knot is one closed, curved line, links are made up of more than one closed, curved line, and they cannot be separated without breaking some lines. Combining two identical patterns on two separate cylinders formed a chain of links (Figure 10).

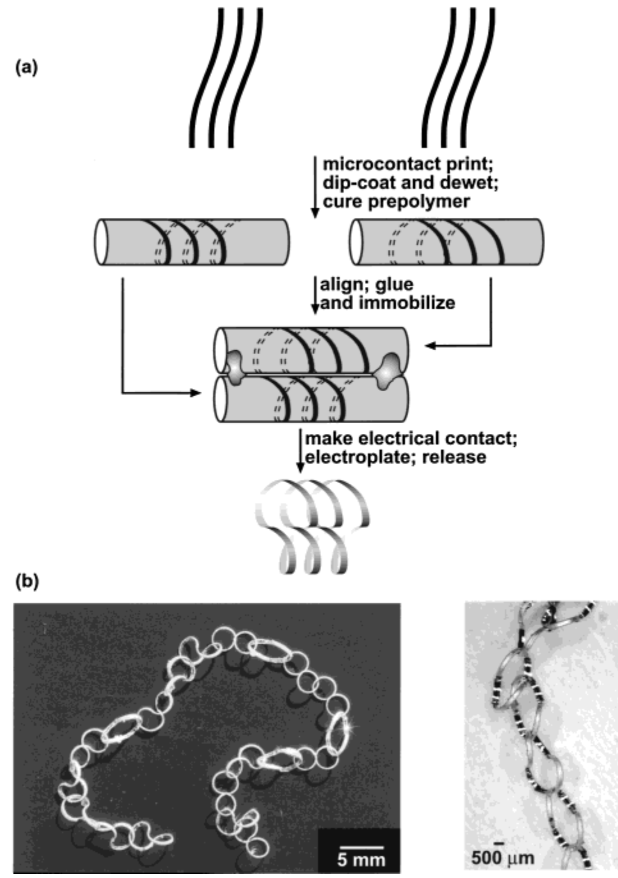


**Figure 10.** (a) Schematic outline of the procedure used to fabricate a chain of links. Starting from two identical patterns (the pattern pair was generated by the procedure shown in Figure 4a), we generated a chain of links by following the procedure described in Figure 8. (b) The left figure shows an optical photograph of a free-joined chain of links in nickel formed by this procedure. Each member of the linked structure shows a different shape in the picture ("8" shape or ellipse shape) because each is positioned differently. The right figure shows an expanded view of a chain of links.

**Borromean Rings.** An example of a more complex linked structure is given by Borromean rings. No deformation of the three component rings can separate them, but if one of them is cut and removed, the remaining two can be separated. Figure 11 illustrates our pattern for Borromean rings and the fabricated structure.

**A Torus.** In addition to knots and links, a wire form for a torus (a donut-shaped surface) can be made by the two-cylinder method (Figure 12). In this structure, two patterned capillaries are joined by semicircular arcs; the resulting structure is topologically a torus, although it is obviously severely distorted from the familiar donut shape.

**A Möbius Strip.** The ability to generate topologically complex, 3D structures by patterning on cylindrical surfaces is not limited to fabricating knots. A Möbius strip is not a structure that can be represented by a graph but is a specially shaped tape. We used two capillaries and a plane to ensure a curve over the whole structure (Figure 13).

## Conclusion

Printing planar patterns on cylinders, and connecting these patterns from the surface of one cylinder to that of the other, allows multiple "over" and "under" crossings and, thus, the fabrication of *any* knot. The procedure is entirely general: it fabricates the topology of any structure of curves that has a

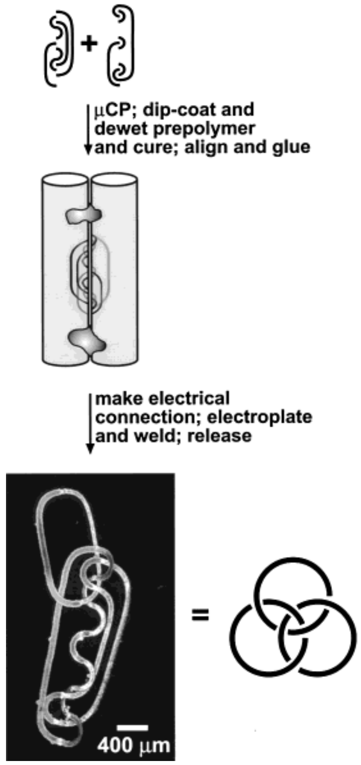


**Figure 11.** Borromean rings fabricated following the procedure in Figure 8. The pattern pair was generated by the procedure described in Figure 4b.

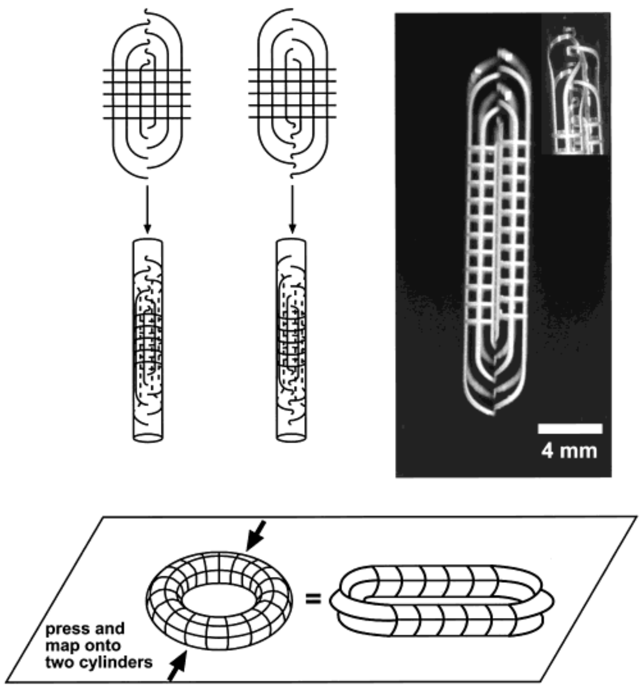


**Figure 12.** A torus. Starting from two mirror-image patterns, we followed the procedure described in Figure 7, and generated a silver torus. The inset figure shows the connection at one end between the two patterns. The diagram at the bottom schematically shows the transformation of a circular torus to a two-cylinder-based torus (in the diagram, we show both tori in a wire form, which are topologically equal).

planar diagram of "over" and "under" crossings. Electrodeposition provides a method that allows metallic structures on different, proximal structures to be joined; in this context, electrodeposition is the equivalent of a weld. This method

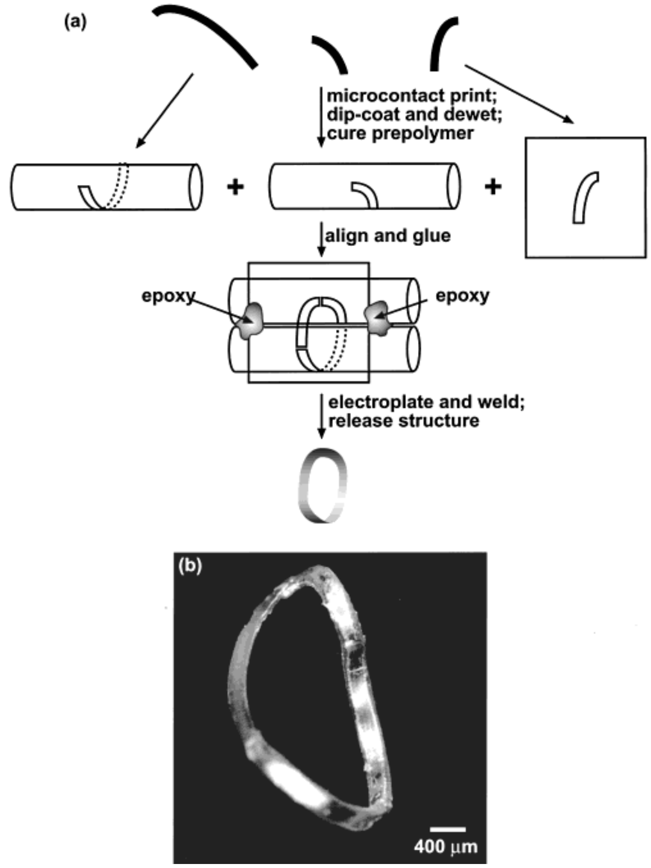


**Figure 13.** (a) Fabrication of a Möbius strip. Fabrication of this structure used two cylinders and a plane. The resulting structure had no discontinuities. We used the procedure in Figure 8 to pattern the two cylinders and photolithography to pattern the planar substrate (a gold-coated glass slide). We first aligned the patterns on the cylinders by using the registration method described in Figure 6, and then, under a stereomicroscope, we aligned the pattern on the glass slide with the patterns on the cylinders. In this figure, the glass slide rests on top of the two cylinders. Electroplating nickel welded the patterns. The structure was released by dissolving the substrates in a aqueous HF solution and the polymer covering it in propylene glycol methyl ether acetate (PGMEA). (b) Optical photograph of a Möbius strip formed by this procedure.

provides a route for fabrication of a broad range of 3D microstructures with complex topologies and topographies.

By patterning two cylinders, we can, in principle, fabricate *any* graph, including any knot (links are interpenetrating knots). This two-cylinder method provides substantial control over topology but less control over distances or geometries within the resulting structures. It is possible to achieve greater control over distances and geometries by using more than two cylinders, by combining cylinders and planes, or by distorting cylinders.

By using more than two cylindrical surfaces, microstructures with other topologies (e.g., the Möbius strip) can be fabricated with smooth, continuous curves. The same topologies can be made with photolithography using three planes of metal with two steps of registration. Structures produced by photolithography will, however, consist of a series of curves in two parallel planes, connected by right angles. The procedure using cylinders provides a different type of control over topology and allows the fabrication of structures composed of smooth curves.

We do not see an immediate application of the specific metallic microknots and related structures generated in this paper. Complex curved shapes do, however, appear in many macroscopic systems—springs, electromagnets, antenna, and stents—and we believe that the methods described here will be useful in the fabrication of complex, 3D microsystems. Complex topologies are also found in polymers and biological macromolecules (for example, some DNA molecules); Seeman has used topological analyses in designing DNA-based knots and tangles.[25−27] We also suggest that the methods for decomposing the complex topologies shown here will be useful in molecular design and synthesis design in circumstances where complex topologies are involved.

## Experimental Section

**Fabrication of Flexible Masks for Photolithography and Stamps for Printing.** A rapid prototyping technique, which can generate features greater than 20 $\mu$m, produced masks for photolithography.[13,17] In this method, we designed a pattern with a CAD program (Macromedia Freehand 8.0). Files containing these designs were sent to a commercial high-resolution printer (5010 dpi) and printed onto transparencies. Using the transparencies as photomasks, we carried out 1:1 photolithography with SU-8 photoresist on silicon wafers by using a Karl Suss mask aligner to produce the masters for producing elastomeric stamps. Negative photoresists (NANO XP SU-8, MicroChem Corp., Newton, MA) were used for photolithography.

The surface of the masters was made more hydrophobic by exposing the silicon wafer to a vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technologies, Inc., Bristol, PA) in a vacuum desiccator to prevent adhesion of the elastomer to the wafer or the photoresist structures during the curing step. The elastomeric stamp for microcontact printing was formed by casting poly(dimethylsiloxane) (PDMS) prepolymer (Sylgard 184, Dow Corning, Midland, MI) against a master and curing the PDMS thermally at 60 °C for about 3 h.[28] The elastomeric stamp was peeled from the master with no apparent damage to the structures in the photoresist.

**Preparation of Glass Substrates.** Planar substrates (glass microscope slides from VWR Scientific, Inc., Media, PA) and cylindrical substrates (glass capillaries from Pyrex, diameter ~2 mm) were cleaned by immersing 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 with distilled water and absolute ethanol. They were finally blown dry in a stream of filtered nitrogen. Using an electron-beam evaporator, we coated these substrates with thin metal layer (titanium (2.5 nm, as an adhesion promoter) and silver (50 nm) for wet-chemical etching; titanium (1 nm, as an adhesion promotor) and gold (10 nm) to control polymer wetting); the capillaries were mounted on a stage that rotated about two orthogonal axes during the evaporation,[29] and this rotating stage allowed metal to be deposited all around the cylindrical substrate in one evaporation. Microcontact printing was followed either by wet-chemical etching or by dip-coating and dewetting liquid prepolymer.

**Microcontact Printing ($\mu$CP) on Planar and Cylindrical Substrates.** We used hexadecanethiol (hexadecyl mercaptan, technical grade, 92%, Aldrich) and dissolved it in ethanol (1 mM) as an "ink" for microcontact printing in this paper. After applying the thiol solution on an elastomeric stamp, we dried the stamp in a stream of nitrogen for ~30 s. For planar substrates, we simply placed the inked stamp in conformal contact with substrates for about 10 s. For the cylindrical substrates, we used a laser-aligned arrangement of precision translation and rotation stages[30] to control the relative orientation of the stamp and substrates, the pressure applied during printing, and the rate of printing. Subsequent wet-chemical etching was accomplished by immersing the printed 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 to remove the un-derivatized silver and by immersing the substrates in an aqueous 1% HF for ~15 s to etch away the exposed titanium.[31]

**Dip-Coating and Dewetting Liquid Prepolymer on Printed Substrates.** After microcontact printing, the silver- or gold-coated substrates were immersed in liquid prepolymer (NANO XP SU-8 2, MicroChem Corp., Newton, MA) and pulled slowly (1 cm/min) from it with a syringe pump (Harvard Equipment, Harvard, MA). The liquid dewetted from the area printed with hexadecanethiol SAM; it covered other areas. Placing the substrates at 90 °C in an oven for an ~5 min "hard bake" converted the liquid into a solid. After electroplating and welding, the solid polymer was removed by immersing in propylene glycol methyl ether acetate (PGMEA) at room temperature for ~10 min.

**Registration.** After silanizing two bare glass capillaries by exposing them to a vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technologies, Inc., Bristol, PA) in a vacuum desiccator, we placed these capillaries close to each other on a flat PDMS piece and glued them by applying 5-min epoxy (Devcon Scientific Yet Simple, Danvers, MA) at the ends. We poured PDMS on them and cured the PDMS in a Petri dish; plastic cuvettes were placed along the side in the dish such that, after curing against the cuvettes, the PDMS mold had smooth side walls. The bare capillaries were removed after cutting of the glued capillary ends and swelling of the PDMS mold in dichloromethane overnight. The PDMS mold returned to its original size after the dichloromethane evaporated on heating in an oven at 50 °C for 2 h. We inserted the patterned capillaries into the PDMS mold. Under an optical stereomicroscope, we rotated the capillaries around their axes and translated them along their axes to align them so that the patterns on the substrates matched to form the desired structure, and we glued the substrates at both ends together with 5-min epoxy when they were still in the PDMS mold. The PDMS mold was cut to release the aligned capillaries for electroplating.

**Electroplating to Weld Patterns on Different Substrates To Produce Topologically Complex 3D Microstructures.** We applied silver epoxy (SPI Supplies, West Chester, PA) to make electrical connections to the metal. In the system generated by dip-coating and dewetting, we first exposed the thin underlying metal by scraping away the cured prepolymer at one end of the capillaries and then applied silver epoxy to these exposed areas. We welded together the patterns on the substrates either by electroplating silver from a silver cyanide-based plating bath (Techni-Silver E2, Technic Inc., Providence, RI) for ~1 h at a current density of ~20 mA/cm$^2$, or by electroplating nickel from a nickel sulfamate-based plating bath (Techni-Nickel "S", Technic Inc., Providence, RI) at ~50 °C for ~1 h at a current density of ~20 mA/cm$^2$. When the procedure based on structures containing thin, sacrificial lines was used, welded structures were released from glass substrates by immersing them in a concentrated aqueous HF (49%) solution.[31] When the procedure based on dip-coating and dewetting was used, welded structures were released from substrates by dissolving the cured prepolymer in PGMEA, thin underlying gold film in an iodine-based gold etchant (GE 8111, Transene Co., Inc., Ravley, MA) for ~5 s, and titanium and glass in concentrated aqueous HF (49%) solution for ~30 min.[31]

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(31) ***Caution*****: HF solution is highly corrosive; the direct exposure of skin to concentrated HF can result in serious damage to skin, tissue, and bones.**