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Biomimetic Fabrication of 3D Structures by Spontaneous Folding of Tapes

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This work explores a strategy for generating functional, three-dimensional (3D) microstructures using (i) photolithography to fabricate micron-scale features, and (ii) self-assembly by spontaneous folding to generate the 3D structure. The strategy has two parts. In the first, we pattern a flexible, polymer tape with metal features and dip-coat these features with solder. On crimping this tape into a quasi-3D shape and joining it to a second flat tape, the structure becomes a linear, quasi-3D structure. In the second part, this structure is allowed to self-assemble into more complex 3D structure by folding; this folding is driven by capillary interactions between the drops of solder. By attaching electronic elements to the uncrimped tape, we demonstrate the generation of an electrically functional device: a self-assembled millimeter-scale 360-degree light detector.

It is difficult to fabricate 3D microstructures with arbitrary shapes. The most versatile methods for 3D microfabrication involve *planar* lithography (using photolithography or soft lithography), printing, or serial writing (using e-beam and focused ion beam or scanning probe), followed by some process (e.g., registration of planar layers or stacking) that adds the third dimension.[1] The techniques for true 3D fabrication currently in use (e.g., surface micromachining, microcontact printing, shell plating, multiphoton polymerization[2]) have limitations, and each provides routes only to specific structures.

We believe that the most practical methods for making *functional* 3D structures with micron-scale patterns will have two steps: *planar* microfabrication using existing technologies to form flat components or wires, and then their transformation into 3D structures. Investment in planar microfabrication has been too large, and the technology has grown too sophisticated and effective[3] to abandon for an entirely new technology that might only marginally improve 3D fabrication.

There is now growing interest in using *folding* as a strategy for 3D microfabrication.[4a−c] Compactness and high volumetric density of functionality have motivated the development of folded, stacked-chip packages. Folding can convert 100-μm-scale 2D structures produced by photolithography into 3D structures using capillary forces or electrical activation of conjugated polymers.[4d−g] To demonstrate self-assembly of simple electronic devices, we have used folding to form electrical connections in 3D between functional elements.[4h,i]

We now demonstrate a use of crimped tapes—folded into 3D shapes via interactions between neighboring faces—to make 3D structures, including a functional electrical device. Our strategy combines the efficiency of existing technologies in planar patterning of flexible substrates with a simple way to transform these functionalized substrates (e.g., organic electronics on 2D substrates, such as displays or E-paper[5]) into 3D structures.

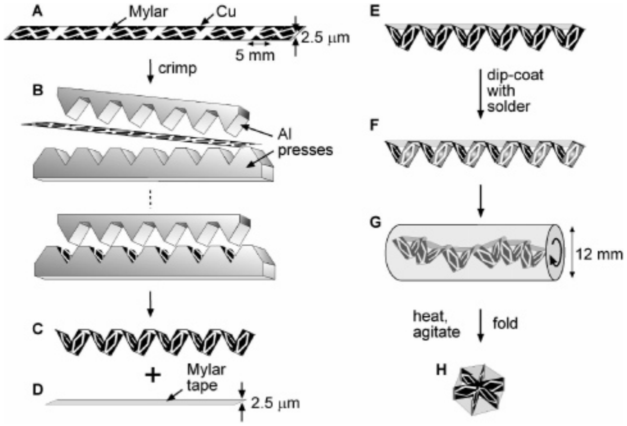

Figure 1. Experimental strategy (see text for details).

The design of this system was inspired by (and loosely modeled on) the folding of biological macromolecules—proteins and RNAs—into functional, globular shapes.[6] In these molecules, the unfolded precursors contain monomers linked to one another in a defined linear sequence ("beads-on-a-string", Figure S1A). The particular 3D structure formed upon folding depends on the sequence of these monomers and on the interactions among them. Our strategy uses the structure of a crimped tape patterned with liquid solder to control the folding of a second flexible tape into a 3D structure (Figure S1B).

We generated a composite of metal and polymer to serve as a rough analogue of a linear peptide by starting with a flat tape patterned with copper features (Figure 1A; for details, see Supporting Information). We crimped this planar tape by pressing it between two metal combs carrying teeth with complementary 3D shapes (Figure 1B); this process generated a string of 3D corrugations (Figure 1C). The crimped tape was joined to the flat tape that we intended to fold in 3D (Figure 1D,E). Attaching the flat tape to the crimped tape (i) maintained the shape of the crimped tape and (ii) provided surface area for mounting electrical components. The patterns of metal were then dip-coated with solder (Figure 1F), and the structure was suspended in water at a temperature above the melting temperature of the solder and agitated gently (Figure 1G). Fusion of droplets of molten solder on neighboring faces of the crimped tape minimized the free energy of the interface between the solder and the aqueous medium and folded the tape into an ordered, 3D structure (Figure 1H). (This process is analogous to minimization of exposed hydrophobic molecular surface during the folding of biological macromolecules.)[6] When cooled and solidified, the solder gave mechanical strength to the final 3D structure and formed electrically conductive bonds. The capillary interactions required for this type of folding can also be based on other types of materials having high interfacial free energy with water (e.g., hydrophobic polymers).[4f]

Figure 2 shows several millimeter-sized structures formed by this procedure, including a functional 3D light detector. We varied two parameters to control the topography of the folded structures:

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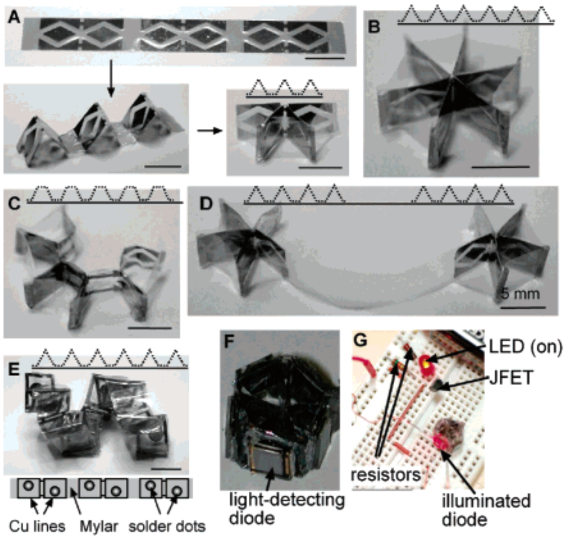

Figure 2. Optical photographs of millimeter-sized structures formed as described in Figure 1. (A) Flat tape with features of copper before and after crimping and of the resulting structure. The inset shows schematically the geometry of the joined crimped and flat tapes before folding. (B−D) Quasi-3D folded structures. (E) A 3D helical structure folded using a tape whose pattern of solder features (lower inset) had S_2 symmetry. (F) A self-assembled light detector. The flat tape bore light-detecting diodes. (G) When illuminated from any angle in the plane, the red LED of the self-assembled light detector emits. See Supporting Information for more details on this device.

the shape into which we crimped the patterned flat tapes (e.g., triangular or trapezoidal corrugations) and the pattern and relative position of features of solder that these tapes carried. When the solder features had mirror symmetry, they overlapped completely during self-assembly without twisting the tapes out of plane; the resulting structures had quasi-3D shapes (Figure 2A−D). When the solder features had S_2 symmetry (i.e., had a center of inversion), they could overlap completely only by twisting the crimped tape out of plane, and the resulting structure had a true 3D shape—the “backbone” of the crimped tape traced out a helix (Figure 2E). Thus, tapes crimped in the same shape could fold into structures of different topology.

For the light detector (Figure 2F), the self-assembly process led to an electrically functional 3D structure that would have been difficult to fabricate by other means. When illuminated with a hand-held red (650 ± 10 nm) laser, current flowed through the light-detecting diode (Figure S1). This current released the gate voltage that blocked current from passing through the light-emitting diode, and red light was emitted. The Supporting Information presents further details of the device.

In this work, we used very simple tapes: “strings” with constant flexibility along the entire length, “beads” of one shape per tape, and nearly identical patterns of solder. The range of 3D structures that can be generated using this strategy can, in principle, be extended when the crimped tapes comprise beads of different shapes and symmetry. In this way, the system can also be designed to allow non-nearest neighbor interactions between individual beads. An interesting question in this context is whether we can induce non-nearest neighbor interactions based on appropriate patterns of solder on the beads, that is, by a form of “pattern recognition” analogous to “shape recognition” between molecules. We have previously demonstrated selective/specific recognition and self-assembly between patterns of different geometry in a system comprising components that were not connected to one another;[7] this problem remains to be addressed in a system comprising components connected in a string.

In conclusion, the structures in Figure 2 demonstrate a new strategy for fabrication of 3D structures based on folding of planar precursors. The system differs in two important ways from previous work. (i) This system is compatible with the commonly used techniques for fabrication of flexible organic electronic devices and thus rests on technology that is already highly developed. The fabrication of the flat tape and of the crimped tape responsible for folding of the structure is entirely decoupled and can, therefore, involve otherwise incompatible processing steps. (ii) In principle, this strategy offers an easy way to incorporate asymmetry in the final 3D structures. The interactions between patterns of molten solder drops are strong: the free energy of the interface between molten solder and water is approximately 400 mN/m[4d] and thus can be used to drive processes (e.g., twisting of the tape) among neighboring beads of the string that might otherwise be disfavored.

While our demonstration incorporates electrical functionality (photodiodes and wires) in the flat tapes, this strategy must achieve structures with (i) high volumetric density of functionality and (ii) smaller dimensions of the tapes if it is to be applied to the fabrication of commercial devices.

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Supporting Information Available: Detailed fabrication and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Moreau, W. M. *Semiconductor Lithography: Principles, Practices, and Materials*; Plenum Press: New York, 1988. (b) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550−575. (c) Gates, B. D.; Xu, Q.; Love, J. C.; Wolfe, D. B.; Whitesides, G. M. *Annu. Rev. Mater. Res.* **2004**, *34*, 339−372.

(2) (b) Madou, M. *Fundamentals of Microfabrication*; CRC Press LLC: Boca Raton, FL, 1997. (b) Kawata, S.; Sun, H.-B.; Tanak, T.; Takada, K. *Nature* **2001**, *412*, 697−698. (c) Lee, W.; Pruzinsky, S. A.; Braun, P. V. *Adv. Mater.* **2002**, *14*, 271−274. (d) Gratson, G. M.; Xu, M.; Lewis, J. A. *Nature* **2004**, *428*, 386−386.

(3) (a) Madou, M. F. *J. Chem. Rev.* **2000**, *100*, 2679−2691. (b) Kovacs, G. T. A.; Maluf, N. I.; Petersen, K. E. *Proc. IEEE* **1998**, *86*, 1536−1551. (c) Campbell, S. A. *The Science and Engineering of Microelectronic Fabrication*, 2nd ed.; Oxford University Press: New York, 2001. (d) Morris, C. J.; Strauth, S. A.; Parvis, B. A. *IEEE Trans. Adv. Packaging* **2005**, *28*, 600−611. (e) Boncheva, M.; Andreev, S.; Mahadevan, L.; Winkleman, A.; Reichman, D. R.; Prentiss, M. G.; Whitesides, S.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **200**5, *102*, 3924−3929. (f) Boncheva, M.; Whitesides, G. M. *Adv. Mater.* **2005**, *17*, 553.

(4) (a) Balde, J. W. *Foldable Flex and Thinned Silicon Multichip Packaging Technology*; Kluwer Academic Publishers: Boston, 2003. (b) Syms, R. R. A.; Yeatman, E. M.; Bright, V. M.; Whitesides, G. M. *J. MEMS* **2003**, *12*, 387−418. (c) Guan J. J.; He, H. Y.; Hansford, D. J.; Lee, L. J. *J. Phys. Chem. B* **2005**, *109*, 23134. (d) Syms, R. R. A.; Yeatman, E. M. *Electron. Lett.* **1993**, *29*, 662−664. (e) Gracias, D. H.; Kavthekar, V.; Love, J. C.; Paul, K. E.; Whitesides, G. M. *Adv. Mater.* **2002**, *14*, 235−238. (f) Clark, T. D.; Boncheva, M.; German, J. M.; Weck, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 18−19. (g) Jager, E. W. H.; Smela, E.; Inganäs, O. *Science* **2000**, *290*, 1540−1545. (h) Boncheva, M.; Gracias, D. H.; Jacobs, H. O.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4937−4940. (i) Boncheva, M.; Ferrigno, R.; Bruzewicz, D. A.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3368−3371.

(5) (a) Tsutsui, T.; Fujita, K. *Adv. Mater.* **2002**, *14*, 949−952. (b) Rogers, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4835−4840.

(6) (a) Alberts, B.; Bray, D.; Lewis, J.; Raff, M.; Roberts, K.; Watson, J. D. *Molecular Biology of the Cell*, 3rd ed.; Garland: New York, 1994. (b) Watson, J. D.; Baker, T. A.; Bell, S. P.; Gann, A.; Levine, M.; Losick, R. *Molecular Biology of the Gene*, 5th ed.; Benjamin Cummings: San Francisco, CA, 2003.

(7) Boncheva, M.; Bruzewicz, D. A.; Whitesides, G. M. *Langmuir* **2003**, *19*, 6066−6071.

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