

quenching to room temperature. As a result, the polarization bandwidth was found to increase by a factor of 2.4 over what was expected of a constant-pitch film. The increased bandwidth was attributed to a pitch gradient resulting from photoinduced racemization of the chiral dopant at the irradiated surface with simultaneous diffusion through the film. This is the first demonstration of a pitch gradient generated in the mesomorphic fluid state and then frozen in a glassy chiral-nematic film.

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Making Negative Poisson's Ratio Microstructures by Soft Lithography**

By Bing Xu, Francisco Arias, Scott T. Brittain, Xiao-Mei Zhao, Bartosz Grzybowski, Salvatore Torquato, and George M. Whitesides*

This paper describes the microfabrication of negative Poisson's ratio (NPR) microstructures using soft lithography.^[1] An NPR material has the counterintuitive property that it shrinks along one axis when compressed along an orthogonal axis. NPR materials have the potential for use as components of microelectromechanical systems

(MEMS) and small mechanical and transducing structures, and as shock absorbers and fasteners.^[2] One of the most promising applications of NPR structures is as matrices for making miniaturized sensors based on piezoceramic composites: incorporation of NPR structures increases both the range of operating frequencies of the piezoelectric transducer and the sensitivity of the device.^[3] It is estimated that NPR materials may enhance the performance of piezoelectric actuators by more than an order of magnitude.^[4–7]

Current approaches to fabrication of NPR structures use inverted honeycomb frameworks,^[8] hierarchical laminates,^[9,10] open cell polymeric or metallic foams,^[11] and mechanical devices made of hinges, springs, and sliding collars.^[12] All of these structures consist of arrays of reentrant cells with cell dimensions larger than 1 mm; all contract under axial compression. Practically, these structures are too soft to serve as mechanically useful matrices in devices.

We wished to fabricate NPR materials “to design”. That is, we wished to specify the geometries and dimensions of the reentrant cell (over the range 10–1000 μm) and its composites and mechanical/electrical properties. The method applied here for the fabrication of NPR materials—soft lithography^[13–16]—has a number of advantages: it can be applied reliably to the fabrication of structures having feature sizes from $>10\ \mu\text{m}$ to 1 mm; it is compatible with a wide range of materials, including polymers and ceramics (by sol–gel methods); it offers a new route to complex metallic microstructures when integrated with electrochemistry,^[17,18] it provides high aspect ratio ($\sim 1:14\ w:h$) structures when a negative photoresist^[19] capable of producing patterns as a thick film is used; it can be used to prepare large (several hundred square centimeters) areas of materials patterned; and it allows fast design-to-test cycles when combined with techniques for rapid prototyping.^[20] Here, we illustrate the fabrication of NPR microstructures with an aspect ratio of up to $\sim 1:14$, and with heights for the walls of the cells of up to $\sim 700\ \mu\text{m}$. The combination of rapid prototyping and soft lithography is a convenient method with which to fabricate NPR test structures, both to optimize their properties and to refine the theories and models describing these properties.

Our design of NPR structures is based on the reentrant cell structures shown in Figure 1-I-c. This structure has orthotropic elastic symmetry and is described by two Poisson's ratios, ν_{xy} and ν_{yx} , defined by Equations 1 and 2, where ε_x and ε_y are the strains in the horizontal and vertical directions, respectively, α is the included angle shown in Figure 1, and a and b are the indicated lengths. These formulae apply when the cell walls occupy a small fraction of the total area. The measurements reported here are for the Poisson's ratio ν_{xy} .

$$\nu_{xy} = -\frac{\varepsilon_y}{\varepsilon_x} = -\frac{\sin^2 \alpha}{(\cos \alpha) (b/a - \cos \alpha)} \quad (1)$$

$$\nu_{yx} = -\frac{\varepsilon_x}{\varepsilon_y} = -\frac{(\cos \alpha) (b/a - \cos \alpha)}{\sin^2 \alpha} \quad (2)$$

[*] Prof. G. M. Whitesides, Dr. B. Xu, Dr. F. Arias, S. T. Brittain, Dr. X.-M. Zhao, B. Grzybowski
Department of Chemistry and Chemical Biology, Harvard University
Cambridge, MA 02138 (USA)
Prof. S. Torquato
Department of Civil Engineering & Operations Research,
and Princeton Materials Institute, Princeton University
Princeton, NJ 08544 (USA)

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Soft lithography offers an effective method to fabricate microstructures with tuned Poisson's ratios, based on cells with designed shapes. Figure 1 shows a series of structures with different unit cells; we expected these structures to have different Poisson's ratios. Structures A–F have NPR. Structures A^[21] and B^[9] have linear walls; structures C–F have curved walls that are intended to clarify the relationship between cell shape and the value of the Poisson's ratio. Structures G and H have positive Poisson's ratio (PPR).

Figure 2 illustrates the process used to fabricate NPR microstructures. An NPR pattern, designed with a computer-assisted design (CAD) program, was transferred into a transparent polymer film using a commercial high-resolution printer (Herkules PRO, 3387 dpi; Linotype-Hell Company). We used the transparency directly as a mask for contact photolithography to create a relief structure in negative thick photoresist (SU-8, MicroChem Corp., Newton, MA); these structures had aspect ratios of up to 1:14 and heights of up to ~600 μm .

To fabricate polymeric or carbon NPR structures, we used three soft lithographic techniques: microtransfer molding (μTM), micromolding in capillaries (MIMIC), and micro-embossing. Each is compatible with a variety of polymers. We made stamps for the fabrication of polymeric NPR structures by casting and curing polydimethylsiloxane (PDMS) against patterned SU-8 photoresist. When a PDMS mold was used in MIMIC, we made its thickness <5 mm to ensure its flexibility; flexibility is important for conformal contact between the stamp and the supporting substrate of the molds. A drop of liquid UV-curable polyurethane (NOA 73, Norland Prod-

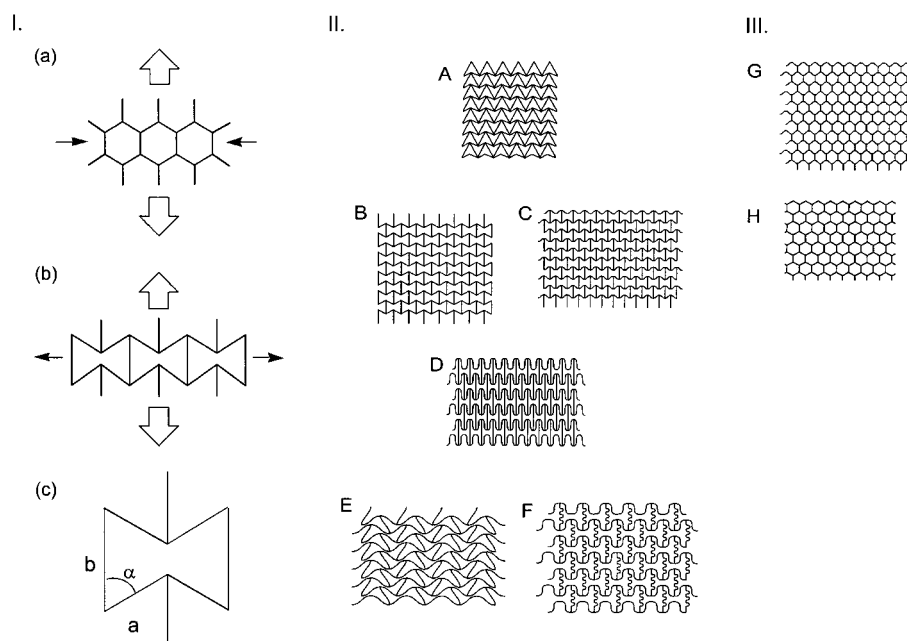


Fig. 1. I a) A two-dimensional honeycomb with a positive Poisson's ratio contracts (small arrows) under a tensile load (large arrows). b) A reentrant honeycomb with a negative Poisson's ratio expands under a tensile load. c) The unit cell of a reentrant honeycomb: a and b are the lengths of the edges, and α is the relaxed angle of the hinges in the absence of loads. II. Microstructures designed to have NPR. III. Microstructures designed to have positive Poisson's ratios (PPRs).

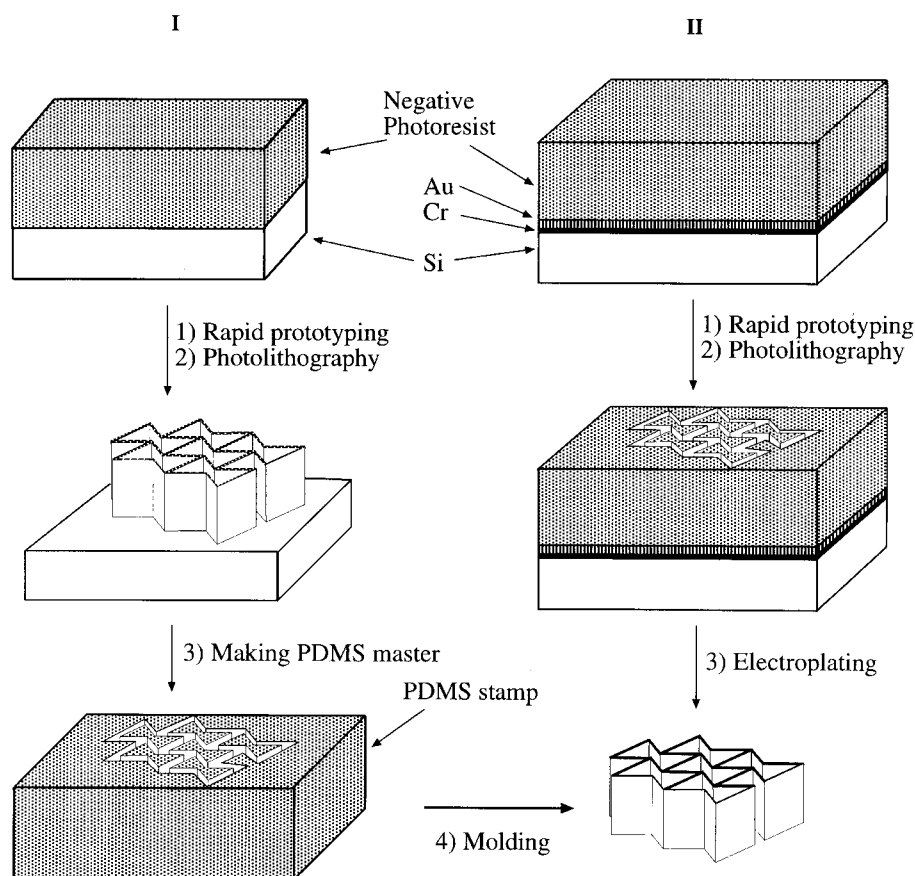


Fig. 2. Schematic representation of the procedures used to fabricate NPR materials.

ucts), when placed on the edge of the mold, filled the channels by capillarity. Exposure to UV light (450 W medium-pressure Hg vapor lamp) for 30 min cured the prepolymer in the filled mold. Figure 3a shows a polyurethane NPR structure made with MIMIC. Larger areas can be fabricated by assisting filling of the mold using vacuum.^[22]

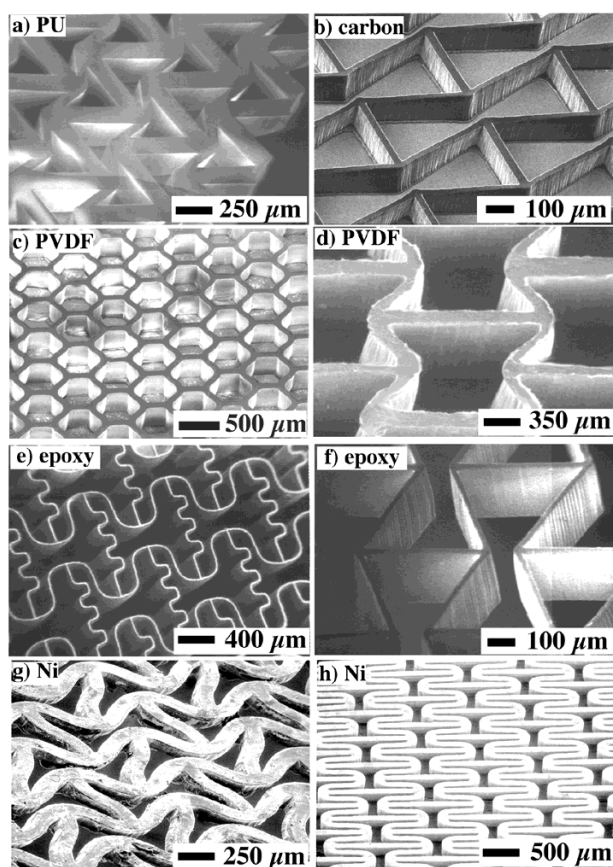


Fig. 3. a,b,d–h) Scanning electron microscopy (SEM) images of NPR microstructures made of various materials: a) polyurethane (aspect ratio of 1:3, height of 325 μm); b) glassy carbon (1:6, 157 μm); d) PVDF (1:8, 420 μm); e) epoxy (1:15, 590 μm); f) epoxy (1:10, 260 μm); g) nickel (1:3, 210 μm); h) nickel (1:3, 260 μm). c) SEM image of a PPR microstructure made of PVDF with aspect ratio of 1:8 and height of 400 μm.

Since the thermal stability and chemical inertness of carbon make it an attractive material as a component in MEMS, we also fabricated glassy carbon^[23] NPR structures. We used μ TM to mold furfuryl alcohol, a carbon precursor, and pyrolyzed the molded microstructure to form an NPR pyrolytic carbon structure (Fig. 3b).

Microtransfer molding and MIMIC work only with liquid prepolymers. In order to apply soft lithography to thermoplastic polymers, we used microembossing, with the PDMS stamp as a pattern transfer element. Polyvinylidene difluoride (PVDF) pellets (Aldrich, $M_w = 180\,000$, $T_m = 170^\circ\text{C}$) were heated above 250°C , compressed between a PDMS stamp and a glass slide with pressure (80 kPa), and then cooled to room temperature. After cooling, separation of the PVDF and the PDMS stamp yielded NPR structures (Fig. 3c and 3d).

The SU-8 photoresist becomes a cross-linked epoxy after exposure to UV light. It is therefore possible to make polymeric microstructures directly from SU-8. To create free-standing epoxy microstructures, we used PDMS as a sacrificial layer.^[24] We spin-coated and cured a thin layer of PDMS on a silicon wafer, and spin-coated SU-8 on top of the PDMS. After exposure and development of SU-8, the PDMS film was dissolved in a solution of tetrabutyl ammonium fluoride (TBAF, 1.0 M in tetrahydrofuran, THF) to produce a freestanding SU-8 structure (Fig. 3e and 3f).

We measured the Poisson's ratios of two representative structures (B and F, both structures fabricated in SU-8). The Poisson's ratio of structure B is described by Equation 1, but no theoretical solution is available for structure F. We found that structure B has a Poisson's ratio of -1.08 , while structure F has a Poisson's ratio of -0.58 (Fig. 4). The wavy "strut" in structure F is in part responsible for the lower absolute value of the Poisson's ratio.

We also fabricated metallic NPR structures since, compared with polymers, metals have higher Young's moduli

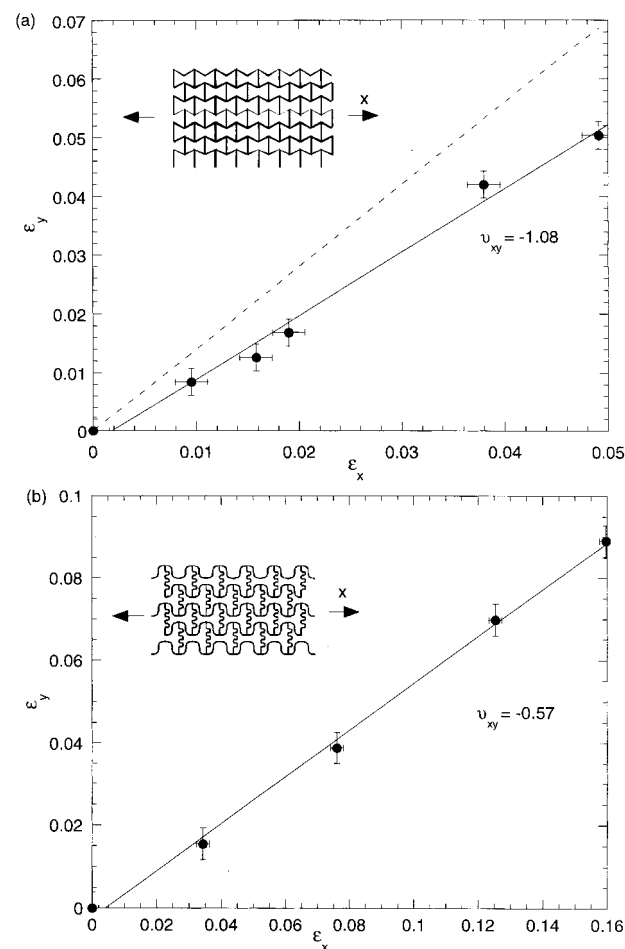


Fig. 4. Strain-strain plots for SU-8 NPR microstructures under load [26]. Arrows indicate the directions, denoted by x, of applied loads; y refers to the in-plane direction orthogonal to x. a) Plot for a structure of the type in Figure 1-II-B. The dotted line indicates the strain-strain curve calculated from Equation 1. b) Plot for a structure of the type in Figure 1-II-F.

(and can therefore withstand higher tensile loads) and are more stable against heat and oxidation. To fabricate NPR structures made of nickel, we electroplated nickel through SU-8 photoresist that was patterned on a gold-coated (200 nm thick) wafer. Figure 3g and 3h show nickel NPR structures with height of $\sim 300\ \mu\text{m}$ and area of $\sim 50\ \text{cm}^2$.

Most of our work concerns planar NPR structures, but three-dimensional (3D) NPR structures are required for some applications. Figure 5-I illustrates the process we used to make a 3D NPR structure. First, we made a PDMS membrane^[25] that has a NPR pattern. Second, the PDMS membrane was coated with gold by thermal evaporation and wrapped around a glass cylinder; care was taken to align the two ends of the membrane. Third, nickel was electroplated on the gold layer. Finally, a freestanding, metallic NPR structure was obtained by dissolving the PDMS using TBAF and removing the cylinder. It is straightforward to extend this approach to other 3D NPR structures.

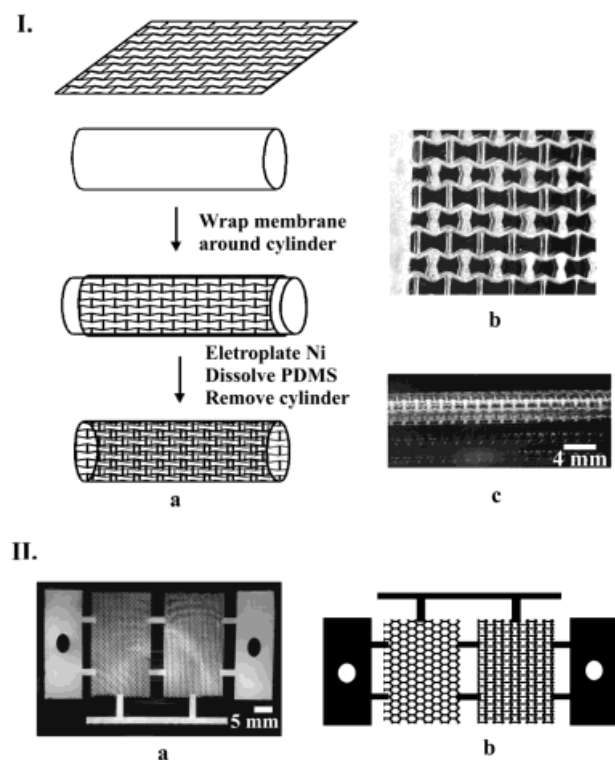


Fig. 5. I. Schematic representation (a) of the process used to fabricate 3D NPR materials: Electrodeposition on a gold-coated PDMS membrane (b) wrapped around a glass cylinder yields a nickel tube with an NPR wall (c). II. A nickel structure (a) of the design (b) composed of both PPR and NPR structures.

We have demonstrated that soft lithography is a useful technique for making NPR structures having features with cell sizes of $100\text{--}500\ \mu\text{m}$, wall thicknesses of $25\text{--}100\ \mu\text{m}$, and aspect ratios of up to 1:14. The combination of rapid prototyping and soft lithography makes it possible to prepare planar and 3D structures with a broad range of Poisson's ratios. An example of a structure that integrates NPR and PPR structures into a designed system is shown in Fig-

ure 5-II. This structure is designed to convert a stress into a tilt (Fig. 5-II-A); Figure 5-II-B shows this structure fabricated in nickel.

The ability of these techniques to accept a range of different materials—polymers, metals, and ceramics—offers the opportunity to combine materials with different Poisson's ratios (as well as different physical properties) with different structures.

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