3D lithography by rapid curing of the liquid instabilities at nanoscale

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Edited by T. C. Lubensky, University of Pennsylvania, Philadelphia, PA, and approved August 1, 2011 (received for review July 6, 2011)

In liquids realm, surface tension and capillarity are the key forces driving the formation of the shapes pervading the nature. The steady dew drops appearing on plant leaves and spider webs result from the minimization of the overall surface energy [Zheng Y, et al. (2010) *Nature* 463:640–643]. Thanks to the surface tension, the interfaces of such spontaneous structures exhibit extremely good spherical shape and consequently worthy optical quality. Also nanofluidic instabilities generate a variety of fascinating liquid silhouettes, but they are however intrinsically short-lived. Here we show that such unsteady liquid structures, shaped in polymeric liquids by an electrohydrodynamic pressure, can be rapidly cured by appropriate thermal treatments. The fabrication of many solid microstructures exploitable in photonics is demonstrated, thus leading to a new concept in 3D lithography. The applicability of specific structures as optical tweezers and as novel remotely excitable quantum dots–embedded microresonators is presented.

A wide variety of lithographic techniques have been developed for fabricating 3D structures (1–5), such as soft lithography (6) that allows one to develop lab-on-chip devices with applications ranging from organic light emitting diode to biology and biochemistry (7). Among others, “capillary-force lithography” is able to nicely pattern polymers at nano-/microscale, but with a very low aspect ratio, in a single step and avoiding the use of external forces (8). Other approaches generate self-patterned structures by using destabilizing forces produced by electric fields, namely electrohydrodynamic (EHD) lithography (9). In EHD lithography, amazing polymeric patterns have been reported, demonstrating the possibility of controlling the process with high accuracy. This method appears suitable only for a few types of periodic patterns having a relatively low aspect ratio (i.e., pillars, dots, and lines). In fact, the control of liquid film instabilities is a demanding task as very little perturbations could drag the nanofluidic system toward nonfully predictable configurations. Such occurrence, for high aspect-ratio features, would prevent the achievement of the expected final steady state. The EHD lithography is usually performed at temperatures above the glass transition of the polymer film [typically polystyrene or poly(methyl methacrylate)], obtaining permanent microstructures by slow annealing and successive cooling, taking hours (10–13).

In general, the hydrodynamic techniques produce steady-state structures resulting from the equilibrium state of a specific fluidic effect. Conversely, the core of our approach consists in “rapid-curing” temporary structures, which evolve continuously under specific fluidic instabilities, by a fast heating procedure. The interesting aspect of this approach is that it gives access to very intriguing fluid shapes, occurring in unsteady fluid physics at nanoscale, which could be very useful in modern science. As investigated recently, breakup of viscoelastic filaments passes through the formation of temporary pearls interconnected by a thin thread, the so-called beads-on-a-string (BOAS) structures (12–14). So a question arises: Is it possible to mimic nature and produce in a controlled way liquid instabilities and stop their “evolution history,” driven by the physics laws? Or, with a popular analogy, is it possible to “freeze” nanofluidic instabilities in polymers as occurs for iced fountain’s jets or the waterfalls in a cold winter?

Here we show a unique but straightforward approach that exploits instabilities and self-assembling of polymeric liquids for fabricating single or arrays of complex high aspect-ratio 3D microstructures. Liquid instabilities are first driven via EHD pressure and then quickly cured to obtain permanent 3D microstructures, by the same thermal treatment, paving the way to a previously undescribed paradigm in fabrication of 3D polymer microstructures. The fabrication of polymer wires, needles, pillars, cones, or microspheres is reported. The polymer structure functionalization through nanoparticles is also shown, and practical proofs of its use in photonics are presented.

Design and Working Principle of the Technique

Our polydimethylsiloxane (PDMS) structures are fabricated through liquid instabilities induced by surface EHD pressure that can commonly be adopted in EHD lithography, in electrospinning processes (15–17) or in a unique approach named pyro-EHD (PEHD) (18). It is important to note that, to the best of our knowledge, EHD or electrospinning has never been used for building up 3D microstructures such as those reported here, having high aspect ratios compared to those obtained through EHD or capillary-force lithography (8, 9).

In our method the air–liquid interface is subjected to an EHD field able to increase the dominant instability, among the natural spectrum of capillary surface waves, at room temperature, without a preliminary annealing process (9). The polymeric permanent structures are generated in our case by rapid cross-linking, which allows us to reduce the overall process duration from hours, required for the glass transition, down to seconds. The combination of high viscosity (12) and rapid cross-linking of PDMS allows us to fabricate structures with aspect ratios extraordinary higher, up to three orders of magnitude, compared to those reported in previous articles (8–10, 19). In fact, the typical aspect-ratio values reported in previous works are in the range of 0.29–0.83, whereas up to 186 is reached here.

The experimental configuration adopted in this work consists basically of a glass slide supporting a sessile nanodrop as liquid reservoir, facing a lithium niobate (LN) substrate at distance D . Any temperature change ΔT of LN causes a variation ΔP_s , which builds up electric charges: The resulting electric field is able to exert an EHD force on the liquid PDMS creating a liquid bridge across the two substrates, as shown in Fig. 1 *A–F* (see *Methods*). The EHD pressure and fluid dynamics cause liquid depletion from the bridge and consequent formation of various temporary liquid silhouettes (12) having the inevitable fate toward the collapsing point (see *Movie S1*).

Author contributions: S.G., S.C., V.V., and P.F. designed research; S.G., S.C., V.V., F.M., and A.F. performed research; S.G., S.C., V.V., F.M., A.F., and P.F. contributed new reagents/analytic tools; S.G., S.C., V.V., F.M., A.F., and P.F. analyzed data; and S.G. and P.F. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1110676108/-DCSupplemental.

Fig. 1. The PEHD system. (A) Scheme of the system. (B–F) Scheme of the temporal evolution of the unstable liquid bridge during the PEHD process, due to the depletion of the liquid and leading to unstable polymer bridges (B) and thinner polymer columns (C and D). (G) Magnified view of other BOAS, (H) example of oblate microspheres, (I) side view of typical BOAS with satellite and subsatellite beads. The first structure on the left has an aspect ratio around 180. (J) Image of polymer microstructure and mechanical compression after the curing process as a proof that microstructures are definitively cured. (K) Elongation and compression of a cured wire with multiple beads.

The dynamic evolutions were observed by a high-speed complementary metal oxide semiconductor (CMOS) camera. Depending on some relevant parameters, such as the amount of liquid (i.e., volume of the patterned reservoir or film thickness), the liquid viscosity, the electric field strength, and the D value, the PEHD instability may reveal different evolutions and scenarios that were possible to draw and understand by means of a systematic experimental investigation, as illustrated in details in *SI Text Sections A* (Table S1) and *B*. Even if, as it is clear by watching the *Movie S1*, the final stage is the collapse and breaking of the nanofluidic silhouette, here we demonstrate that it is possible to freeze the BOAS and other microstructures by a rapid-curing approach.

Spherical and prolate beads along a filament can be obtained as in Fig. 1 *G* and *H*. Typical high aspect-ratio (up to 180) BOAS with satellite and subsatellite beads (12) are shown in Fig. 1*I*. The critical values of the aspect ratios required for producing beads-on-a-string have been estimated to be about 20.

The micro-sized structures of Figs. 1 *G–I* are high aspect-ratio structures fabricated with the “packaged” configuration in which the base and the receiver are joined together at a fixed distance d ranging from 300–500 μm through appropriate thin spacers. For the fabrication of this structure’s PDMS (Sylgard 184, 10:1 mixing ratio base to curing agent), strips of about 10- μm thickness are confined onto the edge of the base by spin coating the sample

at 3,000 rpm for 1 min and successive appropriate accumulation on the edge of the glass slide. The LN wafer, the lid of the package, was stimulated by the hot-air jet for 15 s at 150°C, and successively the package was turned around to put the LN wafer in contact with a cold surface in order to induce a rapid temperature gradient. The “package” was then observed by an optical microscope. Although the nanofluidic instability took place with continuous formation of BOAS, the same hot-air jet was used for curing such structures (typically in about 60 s at 200°C). This process is illustrated in *Movie S2*. This is a typical case where the same thermal source was used for stimulating the pyroelectric effect as well as for the rapid curing of the structures. In this case the structures were formed by the combination of what we named the horizontal and vertical PEHD instabilities. The partial curing sustained by the PDMS during the first hot-air jet (used as pyroelectric stimulus) appears to favor the formation of BOAS within subscenario (4) (see *SI Text Section A*).

The formation and the successive curing process can be monitored in real time as illustrated in *Movie S3*. In fact, it can be clearly visible that, by activating the cure process during the formation of the BOAS, it is possible to fix the structure, avoiding the collapse. In this case the activation of the processes leading to the formation of the microstructures and its subsequent fast curing was obtained using the spotlight of a 150-W halogen lamp

focused onto the microstructures by a parabolic mirror. The temperature of the curing process was about 130 °C.

With the aim to assure that the curing process was fully accomplished, we performed some tests. As shown in Fig. 1J a wire with beads can be elongated up to about 100% of its length. A further example is shown in Fig. 1K where a cured wire with multiple beads, obtained as demonstrated in Movie S4, is also elongated and then compressed to demonstrate the complete curing of the structure without breaking.

In Fig. 2A and B the schematic view of the PDMS patterns (dots and strips) used as reservoirs are shown. Fig. 2C and D shows the top and side microscope images of permanent symmetric bridges obtained by rapid curing of the stationary state. The microsized structures displayed in Fig. 2C and D–H are formed using the packaged configuration with d ranging from 150 to 500 μm and printed separate drops of PDMS as reservoirs. The figures present the top and the side microscope images of permanent symmetric bridges with different aspect ratios, obtained through the rapid curing of the stationary state corresponding to scenario (1). The sample having the LN above the package and in direct contact with the thermal source was heated onto a hot plate at 150 °C for 120 s, activating the PEHD effect and realizing the rapid curing. Two-dimensional arrays of wired

structures, where the PDMS included dispersed multiwalled carbon nanotubes (MWCNTs), are reported in Fig. 2E. PDMS, diluted with hexane (mixing ratio 3 : 1) and with dispersed carbon nanotubes (multiwalled, diameter 110–170 nm, length 5–9 μm , Aldrich Chemistry), was patterned as an array of separate drops. In this case the hot-air jet was used for triggering the nanofluidic PEHD instability as well as for the rapid curing of the structures, in the same conditions described in Fig. 1. The use of MWCNTs makes the curing process faster when compared to the rapid cross-linking using just pure PDMS. The experimental characterization of the curing speed shows an increase of about 25%. This improvement was estimated by testing a sequence of drops with and without dispersed carbon nanotubes. The drops were placed on a glass side and were heated by the hot-air jet for a specific time and the curing stage was checked. In this case a hot-air jet was used for triggering the nanofluidic pyro-EHD instability as well as for the rapid curing of the structures. Conical structures with needle tips, obtained by rapid curing of the Taylor's cone, are shown in Fig. 2F. Essentially such structures consist of two facing cones with different apex angles connected by a thin wire. Fig. 2F shows the conical structures (Taylor's cone) with and without the needle tip formed onto the receiving substrate obtained by unwrapping the package configuration of Fig. 2E.

Fig. 2. Structures obtained with patterned reservoirs droplets and films. (A and B) Schematic view of two typical reservoir geometries consisting of arrays of single drops and aligned strips of PDMS, respectively. (C and D) Soft solid-like bridges with different aspect ratios (0.36 and 0.88, respectively). (E) Solid-like wired structures connected by conical terminations. (F) Conical structures with and without needle tip. (G) Self-assembled multiple jets. (H) Array of bridges obtained from PDMS strips including MWCNT to improve the heat diffusion into the polymer. (I) Extended focus image of the cured BOAS structures and large and magnified view of another cured BOAS structure. (J) Side view of periodic solid-like wires. The aspect ratio is around 60.

Moreover, Fig. 2*G* reports a typical multiple, self-arranged, jetting effect in a liquid film (see [Movies S5](#) and [S6](#)), from which multiple periodic structures can be fabricated, such as the 2D array of columns. The experimental characterizations are reported in details in [SI Text Section B](#) and in [Fig. S1](#). Fig. 2 *H–J* show a linear array of cured BOAS and wired structures, respectively. Fig. 2*J* shows well-ordered high aspect-ratio structures fabricated with the separate configuration, in which the base and the receiver were mounted onto two separate vertical translation stages in order to change finely the distance d . The separate configuration provides higher flexibility and thus enables the implementation of a wider variety of test experiments, whereas the packaged one is more compact. The LN wafer was stimulated by the hot tip and, after about 3 s, the typical multiple jetting of PDMS [scenario (2)] began and was rapid-cured by the hot-air jet applied at 200 °C for 60 s.

It is important to note that, compared to electrospinning studies (17) where BOAS are generated and controlled, our approach is based onto a process evolving under the Rayleigh instability but with a nonconstant Deborah number due to varia-

tion of the viscoelastic properties of the PDMS during the process. In fact, differently from other electrospinning methods, our approach uses a thermal load that changes the liquid properties during the process, thus leading to different shapes of the liquid jet from simple uniform wires to BOAS structures.

Applications of Rapid Cured PDMS Microstructures

The wires are potential optical waveguides similar to optical fibers and could be used for collecting or distributing light signals (see Fig. 2 *E* or *J*) in lab-on-a-chip optofluidic devices, whereas that shown in Fig. 1*D* can be used as optical tips able to deliver or collect light in scanning probe microscopes [i.e., scanning near-field optical microscopy (SNOM)].

Optical Tweezers by Bessel Beams. The cone (see Fig. 1D) is a valuable optical lens, named axicon, a layer of PDMS polymer diluted with hexane (mixing ratio 3 : 1 PDMS/hexane) was spin-coated on a microscope slide at 3,000 rpm for 1 min. The dilution was adopted with the aim to obtain thinner layers by the spin-coating process. Thin spacers of 100 μm were glued on the edges of the base to superimpose the LN plate at a fixed distance. The sample

Fig. 3. Optical trapping application. (A) Microscope image of the fabricated PDMS microaxicons. (B) A Gaussian beam passing through an axicon becomes a Bessel beam. (C) A section of the Bessel beam at about $Z_{\max}/2$, with the typical rings. (D) The numerical amplitude reconstruction along the propagation path of the Bessel beam exiting the axicon; reconstructed phase map of the beam in C (*Inset*). (E) Sketch of the setup for multiple trapping. (F) Frame of [Movie S4](#) showing six microspheres trapped in different positions along the axicon line of focus direction (i.e., along the z axis), forming a sort of “snake” while moved in the x - y plane. (*Inset*) Magnified view of the first three trapped particles.

shell QDs. Samples of degassed PDMS with CdSe QD nanocrystals were prepared by mixing 3 mL of PDMS with 300 μL of Lumidots CdSe 590 nm (5 mg/mL concentration in toluene, fluorescence emission maxima spanning the visible spectrum, Sigma-Aldrich). The mixtures were obtained by vacuum-stirring in order to vaporize the solvent (toluene), making easier the curing process. A mixture droplet was placed on a glass slide and the auxiliary LN plate was mounted on independent vertical translation stages (separate configuration) to control the distance D while PDMS wire-structures were in progress. The curing process was obtained by a lamp as in case of Fig. 1J.

The fabricated 3D arranged beads can be remotely excitable without requiring distributed Bragg reflectors, as in case of the recent QD-embedded hemispherical structures in ref. 24. Fig. 4B and C shows the top and the side view, respectively, of the typical fluorescence effect induced into a QD-embedded frozen PDMS bridge, excited by a continuous-wave laser emitting at 325 nm. Bright rings along the rim of the bridge correspond to the formation of a preferential WGM due to the axial symmetry of the structure (26). The QD-embedded microsphere in Fig. 4D exhibits homogeneous photoluminescence. Fig. 4E shows the fluorescent image of a wire with uniform and stable photoluminescence during UV scanning (see [Movie S9](#)). Fig. 4F and G show QD-embedded BOAS excited by a UV lamp. In Fig. 4H–K the emission of conical structures during UV scanning is shown. The brighter regions in the periphery are attributed to resonant modes corresponding to different wavelength emissions (see [Movie S10](#)). Moreover, the well-known softness of PDMS would provide additional tuning functionality. In fact, as demonstrated in Fig. 1J and K, the cured microstructures can be mechanically stretched thus causing a change of the spherical shape. This is an important feature when WGM optical microresonators are applied for sensing purposes. Dynamic behavior can be nicely observed in [Movies S3](#) and [S4](#).

The fabrication process is easier to accomplish than other methods, where QDs are embedded into the periphery of polymer microspheres through complicated chemical procedures (24), enabling the inclusion of the QDs into deeper regions of the structures.

In conclusion, “Mother Nature” shapes liquid configurations during the evolution of liquid EHD instabilities, whereas a facile and rapid-curing process can produce microphotonic elements

—a sort of natural nanofluidic “optics foundry.” Multiphase structures are fabricated through the appropriate dispersion of solid particles into the PDMS layer. The ability to fabricate fibers with BOAS and diameter on the micrometer scale gives the opportunity to engineer scaffolds at microscale. Once the scaffold is created, using the rapid-curing process reported here, its surface could be useful for tissue engineering or drug delivery by functionalizing it (28), thus avoiding problems related to the high temperature required for during the fabrication process.

We believe that further theoretical investigations (12), in combination with the simple rapid-curing approach demonstrated here, will allow in the future the development of a previously undescribed “3D lithography concept/platform,” in which nanofluidic instabilities could be “fluidynamically” designed a priori with the aim at fabricating even more complex shapes exploitable in many fields.

Methods

Lithium Niobate Crystals. The LN crystals used for the pyroelectric effect were z-cut single domain wafers optically polished on both sides (by Crystal Technology Inc.), with 3-inch diameter and 0.5-mm thickness.

Heat Sources. The hot-air gun, used for cross-linking rapidly the PDMS fluidic structures, had an operation temperature ranging from 50 to 660 $^{\circ}\text{C}$ (discrete steps of 10 $^{\circ}\text{C}$) and an air volume throughput in 10 stages between 250 and 500 L/min. The hot tip of a conventional soldering iron, used as a contact thermal stimulus for the pyroelectric effect, had a maximum operation temperature of 250 $^{\circ}\text{C}$.

The Pyroelectric Effect. At equilibrium, the spontaneous polarization P_s of the LN crystals is fully compensated by the external screening charge and no electric field exists (29). When the crystal is subjected to a temperature variation ΔT , the spontaneous polarization P_s varies and, neglecting the losses, an uncompensated surface charge $\sigma = P_s \Delta T$ builds up. Therefore an electric field appears across the z surfaces. In case of LN at 25 $^{\circ}\text{C}$, the pyroelectric coefficient P_c is equal to -8.3×10^{-5} C/ $^{\circ}\text{C}/\text{m}^2$.

Imaging Setup. The illumination equipment consisted of a conventional blue collimated led (wavelength of 470 nm and beam power around 400 mW) equipped with a neutral density filter. A 5 $\times$ microscope objective was used for visualizing the PDMS instabilities onto a CMOS camera. The camera had a pixel area of $(12 \times 12) \mu\text{m}^2$ and was able to capture 125 frame s^{-1} with a resolution of $(1,280 \times 1,024)$ pixel 2 .

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