3D lithography by freezing unstable liquid shapes

Pietro Ferraro, Simonetta Grilli, Andrea Finizio, Francesco Merola, Sara Coppola, and Veronica Vespini

Rapidly curing unsteady nanoscale structures in polymeric liquids results in solid microstructures that could be used as photonic elements.

In the realm of liquids, surface tension and capillary forces drive the spontaneous formation of shapes. Because of surface tension, these spontaneous shapes have very good spherical curvatures and hence desirable optical properties. They could be exploitable for photonic applications and other fields of modern science.

A variety of fascinating structures also evolve continuously in liquids under instabilities that occur at the nanoscale in non-equilibrium conditions. These shapes are intrinsically short-lived. However, we have found that it is possible to freeze such nanofluidic instabilities in polymers as occurs with fountain jets or waterfalls in a cold winter. Using this method, we have fabricated complex 3D microstructures singly and in arrays.

The approach exploits the instabilities and self-assembly of polymeric liquids. It also relies on the pyroelectric effect, which is the ability of certain materials to generate an electrical field when they are heated or cooled. We used this effect for generating liquid instabilities in polymers and then quickly curing them to obtain permanent constructs.

The same thermal technique is used to drive and then rapidly cure liquid instabilities. The name of the technique, pyro-electrohydrodynamic lithography, refers to the generation of structures using forces produced by electrical fields that are generated by the pyroelectric effect. We have reported the fabrication of polydimethylsiloxane (PDMS) wires, needles, pillars, cones, and microspheres, and also presented practical proof of their use in photonics.

The experimental configuration consists of a glass slide supporting a sessile PDMS nanodrop as a liquid reservoir, facing a lithium niobate (LN) substrate at distance D. Any temperature change of LN builds up electrical charges through the pyroelectric effect. The resulting strong electrical field exerts a force on the PDMS drop, creating a bridge across the two substrates (see Figure 1). The fluid dynamics depletes liquid from the unstable

Figure 1. Experimental procedure for 3D microstructure fabrication. (1) System scheme. (2–6) Temporal evolution of an unstable liquid bridge during the pyro-electrohydrodynamic process, leading to the formation of a polymeric (3) pillar, (4) cone, and (5–6) microspheres on a wire. LN: Lithium niobate.

Figure 2. Frozen microstructures. (a) Bridges with different aspect ratios, (b) beads-on-a-string (BOAS) structures, (c) wires connected by conical terminations, and (d) conical structures with and without needle tip.

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bridge and thus forms various temporary liquid silhouettes. We observed these dynamic evolutions using a high-speed CMOS camera imaging system. The final stage of such an unstable column is its collapse, but we are able to freeze the microstructures by rapid-curing. The same hot-air jet that stimulates the generation of structures by heating the LN also rapidly cures them, typically in about 60 s at 200 °C (see video2). Figure 2 shows some of the frozen microstructures, such as bridges with different aspect ratios, wired structures connected by conical terminations, conical structures with and without needle tips, and beads-on-a-string (BOAS) structures.

These structures could find application in different fields. For example, the wires are potential optical waveguides, similar to optical fibers, that could be used for collecting or distributing light signals. The cone in Figure 2(d) is a conical ‘axicon’ lens used for imaging and generating Bessel beams. We used this structure in combination with a laser source as optical tweezers3—see Figure 3(a)—that can trap and move micrometric latex particles: see video.4 The BOAS may be used for sensing applications and either as passive or active optical microresonators. As active elements, we successfully embedded cadmium selenide microspheres inside the BOAS, and excited them with a UV laser: see Figure 3(b) and (c).3

We believe that further theoretical investigations, in combination with the simple rapid-curing approach demonstrated here, will allow future improvements toward a new 3D lithography platform, in which nanoliquid instabilities could be fluid dynamically predesigned with the aim of fabricating even more complex shapes exploitable in many fields.

References
Generation, curing, and testing of a BOAS. Credit: INO Group.
Optical tweezing experiment. A 10 μm-sized latex particle is trapped and moved by the focused laser light (in green) generated by a PDMS microaxicon (whose base is shown by the purple circle). Credit: INO Group.