NANOFABRICATION

Nanoscale printing simplified

Pyroelectric effects can be used to create attolitre droplets of liquid without the use of complicated electrodes, high-voltage circuits or nozzles, thus opening up new directions for printing and patterning substrates.

John A. Rogers and Ungyu Paik

Techniques for printing patterns with liquid inks have their origins in the earliest days of human civilization. One of the most prevalent forms today is the desktop inkjet printer, in which localized heating leads to the controlled formation and ejection of small droplets of ink at rates of tens of thousands per second. This technology, which provides a resolution of several tens of micrometres, plays a major role in printing for the graphic arts.

It is also possible to use electric fields to draw narrow jets of liquids from fine apertures[1] in a process that was first studied in experimental detail by Geoffrey Taylor[2] in 1964. Writing in *Nature Nanotechnology*, Pietro Ferraro, Simonetta Grilli and colleagues[3] of the Italian National Institute of Optics describe a clever approach to use these basic phenomena for a type of inkjet printing that offers nanoscale precision and operational features that overcome many of the limitations of previous strategies.

When implemented with pens based on micro- or nanoscale glass capillaries, the electrohydrodynamic effects studied by Taylor enable printing with resolution approaching 100 nm using pigments and a variety of advanced materials, such as conducting polymers, single-walled carbon nanotubes, oligonucleotides and colloids[4–6]. This capability has created new opportunities for printing in areas of technology and manufacturing. For example, there is growing interest in the development of electrohydrodynamic-jet (e-jet) printing techniques for applications in electronics, optoelectronics and biotechnology, where high-resolution patterning of functional materials in liquid form has the potential to provide advantages in cost and capabilities over established methods such as photolithography.

The Italian team built on this e-jet approach with a concept that relies on the well-known pyroelectricity effect that occurs in polar crystals such as lithium niobate. Here, heating induces a polarization that leads to uncompensated charges on the surface of the niobate substrate. This process, illustrated in Fig. 1, creates local potentials that can reach into the kilovolt range, even for mild increases in temperature. These electric fields have been used in the past to manipulate fluids through electrowetting, as an example, for devices such as tunable liquid microlenses[7]. Ferraro, Grilli and co-workers show that when the niobate substrate is placed near a second substrate that supports ink droplets or films of liquid, the pyroelectric effect in the niobate substrate can initiate electrohydrodynamic responses. In fact, when the electric fields exceed a critical magnitude, pulsating jets emerge, pulling the liquid from the substrate in the form of a rapid 'machine gun' succession of fine droplets with repetition rates of 50–275 times per second, depending on whether the liquid is a droplet or a film. The high-speed movies provided in their Supplementary Information allow direct visualization of these interesting effects.

These pulsations continue until the fields dissipate on cooling of the pyroelectric niobate material, and the ejection of the droplets can therefore be reversibly turned on and off in this manner. The spatial location of this ejection can be controlled simply through the position of the heat source, which could be a focused laser beam or the hot tip of a soldering iron (Fig. 1). The heating creates a sort of 'virtual nozzle' through localized electrohydrodynamic effects, thereby omitting the need for actual nozzles. With rapid scanning of the hot tip or with spatial modulation of the laser, one can envisage a programmable source of such virtual nozzles for high-throughput patterning, without the need for high-voltage power supplies or electrodes of any type. The Italian team showed that printing can occur either directly onto the pyroelectric niobate crystal or, more practically, onto a dielectric plate inserted between the crystal and the substrate that supports the ink.

With this method, several patterns of dots and lines were printed using inks ranging from almond oil to poly(dimethylsiloxane); multiphase materials such as carbon nanotubes and cell-cultivation media dispersed in oil can also be used. In systematic experiments, it was found that by reducing the sizes of the ink droplets, the sizes of the printed features can be decreased by a corresponding amount. For the smallest ink droplets, printing resolution down

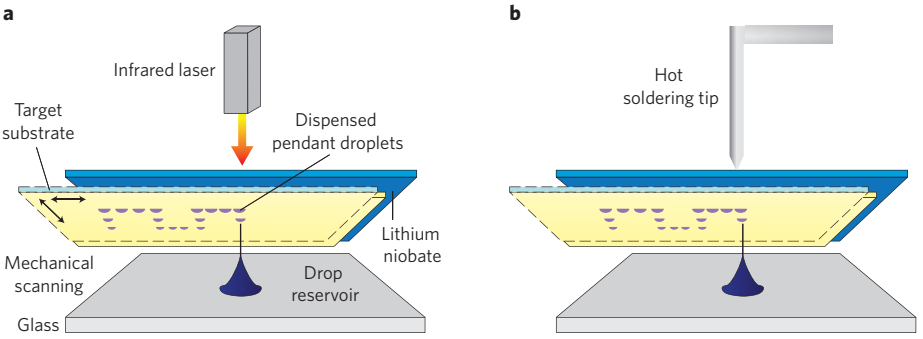

Figure 1 | Schematic illustration of a pyroelectric approach to e-jet printing. In this process, a laser (**a**) or a hot soldering tip (**b**) causes heating in a slab of pyroelectric material such as lithium niobate (blue). This heating creates local electrical potentials that initiate electrohydrodynamic effects in a thin layer of ink on an opposing glass substrate (grey). These effects lead to the ejection of small droplets that are printed (purple), with nanoscale resolution, onto an intervening target substrate (yellow).

to 300 nm (corresponding to attolitre volumes) was achieved. This approaches some of the best results reported using nanocapillary nozzles[4,5], and greatly exceeds the possibilities provided by conventional inkjet methods.

The versatility of the pyroelectric approach to e-jet printing, the simplicity afforded by the absence of nozzles, electrodes or high-voltage power supplies, and the potential for high-speed printing collectively make the method very attractive for many applications. Opportunities for future work seem to lie in developing methods for preparing optimized configurations of the ink (for example, controlling the size of the droplets or the thickness of the films) for printing and for replenishing this ink as it is consumed during printing. The physics of thermal diffusion and related processes that determine the upper limits in patterning speeds might also be interesting to explore.

As an alternative to pyroelectrics for generating local fields, one could also consider programmable arrays of patterned electrodes or scanning metal probes as routes to virtual nozzles. Pursuing these possibilities, exploring advanced inks and exploiting the capabilities for applications in biology, printed electronics and related areas all represent promising directions for further research. ❐

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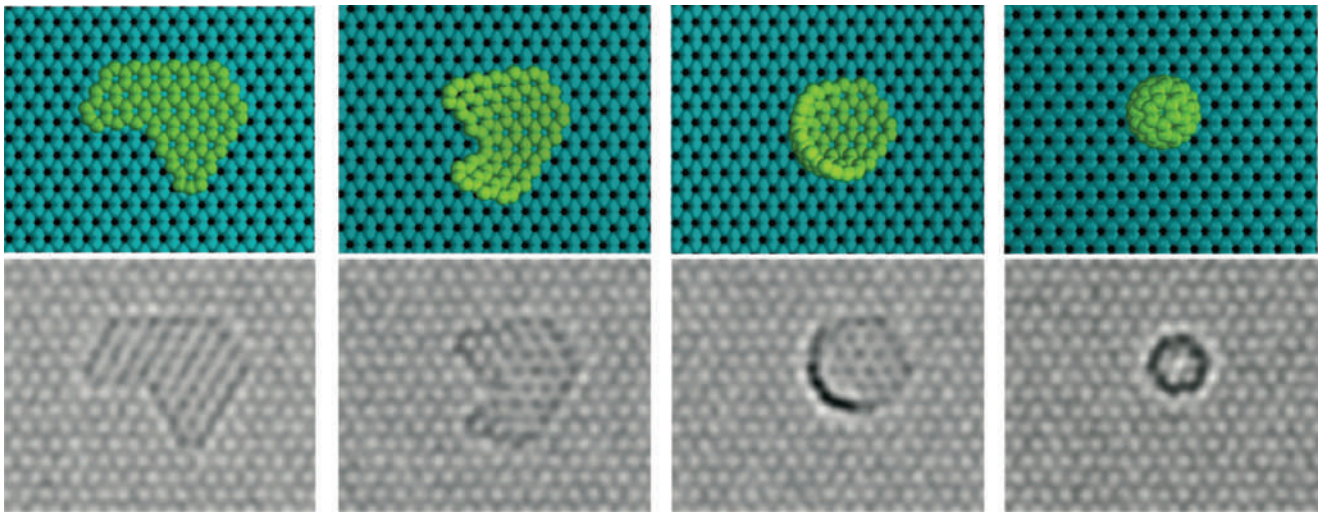
References

1. Collins, R. T. *et al. Nature Phys.* **4,** 149–154 (2008).
2. Taylor, G. I. *Proc. R. Soc. Lond. A* **280,** 383–397 (1964).
3. Ferraro, P., Coppola, S., Grilli, S., Maturzo, M. & Vespini, V. *Nature Nanotech.* **5,** 429–435 (2010).
4. Park, J-U. *et al. Nature Mater.* **6,** 782–789 (2007).
5. Park, J-U. *et al. Nano Lett.* **8,** 4210–4216 (2008).
6. Poon, H. F., Saville, D. A. & Aksay, I. A. *Appl. Phys. Lett.* **93,** 133114 (2008).
7. Miccio, L. *et al. Opt. Lett.* **34,** 1075–1077 (2009).

FULLERENE SYNTHESIS

Caught on camera



Graphite is routinely transformed into fullerene C_{60} molecules with the help of lasers or electric arcs, although the exact mechanism by which these spherical carbon structures are formed is still unclear. Andrey Chuvilin, Andrei Khlobystov and colleagues at the universities of Ulm and Nottingham have now directly imaged the formation of fullerene molecules from graphene (a single layer of carbon atoms) with an aberration-corrected transmission electron microscope (*Nature Chem.* **2,** 450–453; 2010).

The Ulm–Nottingham team fired an 80-keV electron beam at their starting material, exciting the carbon atoms and fragmenting the graphene sheet into smaller flakes. These flakes underwent a series of further changes before finally forming a spherical fullerene molecule that seemed to roll back and forth on the graphene substrate below. The high-resolution imaging was supplemented with quantum mechanical modelling, which helped the team determine the formation mechanism.

The figure shows models (top) and simulated electron-microscopy images (bottom) of key stages in the mechanism. Chuvilin, who is now at the nanoGUNE laboratory in Spain, and colleagues found that the electron beam removed carbon atoms from the edges of the graphene flakes (left), destabilizing the flakes and leading to the formation of pentagons (middle-left). This in turn caused the flakes to curl and form bowl-shaped structures (middle-right). Finally, the edges of the flakes were 'zipped up' to yield the fullerene molecules (right).

The conditions under which these molecules were formed is markedly different from those normally used for fullerene production, so 25 years after C_{60} was first produced in the laboratory, there is still more to learn about the mechanisms used to produce it.

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