industry to safeguard equine welfare in the Grand National steeplechase.

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Microperiodic structures

Direct writing of three-dimensional webs

Applications are emerging that require the creation of fine-scale structures in three dimensions — examples include scaffolds for tissue engineering[1], microfluidic devices[2] and photonic materials that control light propagation over a range of frequencies[3]. But writing methods such as dip-pen nanolithography[4] and ink-jet printing[5] are either confined to two dimensions or beset by wetting and spreading problems. Here we use concentrated polyelectrolyte inks to write three-dimensional microperiodic structures directly without using masks. Our technique enables us to write arbitrary three-dimensional patterns whose features are nearly two orders of magnitude smaller than those attained with other multilayer printing techniques[6].

For this direct-write process, we have developed fluid inks that flow readily through fine deposition nozzles and solidify rapidly in a coagulation reservoir (Fig. 1). The inks are made up of concentrated polyelectrolyte complexes that consist of non-stoichiometric mixtures[7] of polyanions (polyacrylic acid, PAA) and polycations (polyethylenimine, PEI, or polyallylamine hydrochloride, PAH). By regulating the ratio of anionic (COO^-Na^+) to cationic (NH_x^+) groups and combining these species under solution conditions that promote polyelectrolyte exchange reactions[8], we produce homogeneous fluids (40–50 wt % polyelectrolyte in aqueous solution; for methods, see supplementary information) with the requisite viscosity (about 5–150 pascal seconds) for deposition through microcapillary nozzles of varying diameter (0.5–5.0 μm).

When deposited in an alcohol/water coagulation reservoir, these concentrated polyelectrolyte inks coagulate to form self-supporting filaments or rods (Fig. 1). The reservoir composition strongly affects both the ink's elasticity and the coagulation mechanism, which is driven by electrostatic effects in water-rich reservoirs and by solvent effects in alcohol-rich reservoirs. For example, the elasticity of PAA/PEI ink (ratio of anionic/cationic groups: $[COO^-Na^+]/[NH_x^+]=5.7$) rises dramatically from 1 Pa (fluid phase) to nearly 10^5 Pa (coagulated phase) upon deposition in a reservoir containing 83–88% isopropyl alcohol. Under these conditions, the deposited ink filament is elastic enough to retain its shape while being able to flow and adhere to the substrate and underlying patterned layers.

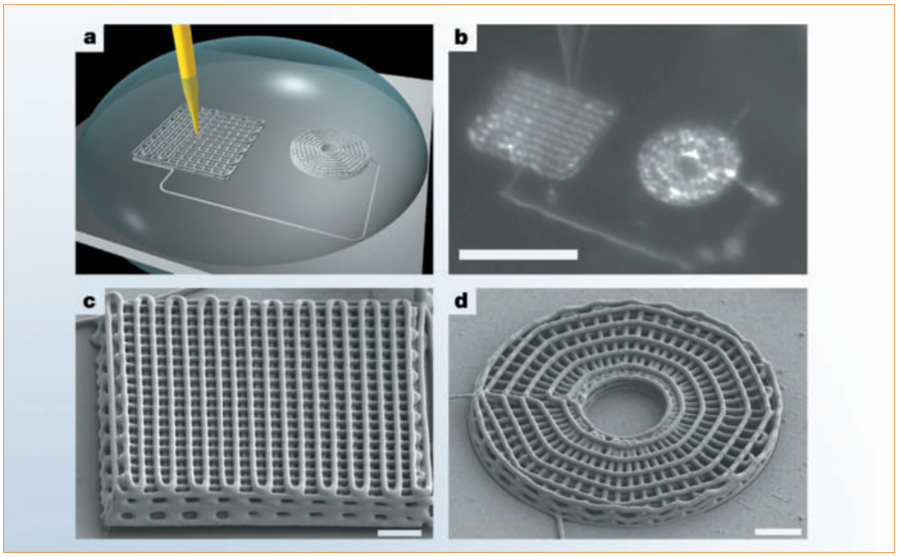

Figure 1 Direct-write assembly of three-dimensional microperiodic structures. **a,** The ink-deposition process (not drawn to scale). A concentrated polyelectrolyte ink is housed in a syringe (yellow) immersed in a coagulation reservoir (grey hemispherical drop) and deposited on to a glass substrate (light grey). **b,** Optical image acquired *in situ* during deposition reveals the features drawn in **a**, including the deposition nozzle that is patterning a three-dimensional lattice, as well as a completed radial array. This image is blurred by the reservoir (scale bar: 100 μm). **c,** Three-dimensional periodic structure with a face-centred tetragonal geometry (filament diameter: 1 μm; 10 layers; scale bar: 10 μm). **d,** Three-dimensional radial array (filament diameter: 1 μm; 5 layers; scale bar: 10 μm).

Images of three-dimensional microperiodic lattices and radial arrays assembled from the PAA/PEI ink are shown in Fig. 1c, d. These structures can have solid or porous walls and rod-like filaments that span the web, as well as tight and broad-angled features. A three-axis (x,y,z) micropositioning device deposits the ink, sequentially building layered, patterned structures (see supplementary information). After producing a two-dimensional patterned layer, the nozzle is raised in the z-direction to generate the next layer. The process is repeated until the full three-dimensional structure is fabricated (building time is about 5 min).

The versatility of these inks is demonstrated by microperiodic structures made from PAA/PAH ink ($[COO^-Na^+]/[NH_3^+]=0.5$), which consist of a patterned array of polyelectrolyte filaments with a net positive surface charge (see supplementary information). These three-dimensional polyelectrolyte scaffolds open up new opportunities for the electrostatic layer-by-layer assembly[9] of materials, which has previously been limited to thin-film[9] or discrete colloidal structures[10].

Direct-write assembly is a powerful way to create three-dimensional microscale structures of arbitrary design and functionality. A variety of inks could be developed using other polyelectrolyte mixtures, based for example on biologically, electrically or optically active polyelectrolytes. The structures created could direct cell-scaffold interactions[11], manipulate fluid flow[2], control light propagation[3], or respond to environmental stimuli[12].

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