Direct writing in three dimensions

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The ability to pattern materials in three dimensions is critical for several emerging technologies, including photonics, microfluidics, microelectromechanical systems, and biomaterials. Direct-write assembly allows one to design and rapidly fabricate materials in complex three-dimensional shapes without the need for expensive tooling, dies, or lithographic masks. Here, recent advances in ink and laser writing techniques are reviewed with an emphasis on the push toward finer feature sizes. Opportunities and challenges associated with direct-write assembly are also highlighted.

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New methods for materials fabrication at the micro- and nanoscale will drive scientific and technological advances in the areas of biology, chemistry, materials science, and physics. The broad diversity of potentially relevant materials, length scales, and architectures underscores the need for flexible patterning approaches. One important example is the fabrication of three-dimensional periodic structures comprised of polymeric[1-3], colloidal[4], or semiconductor[5] materials. These structures may find potential application as tissue engineering scaffolds[6], drug-delivery devices[7], microfluidic networks[8], sensors[9], and photonic band gap materials[10]. Several strategies have recently emerged for precisely assembling three-dimensional periodic arrays[1-5], including standard lithographic[5], colloidal epitaxy[4], and direct-write techniques[1,3]. Of these, only the latter approach offers the materials flexibility, low cost, and ability to construct arbitrary three-dimensional structures required for advances across multidisciplinary boundaries.

The term 'direct-write' describes fabrication methods that employ a computer-controlled translation stage, which moves a pattern-generating device, e.g. ink deposition nozzle or laser writing optics, to create materials with controlled architecture and composition. Several direct-write techniques have been introduced that are capable of patterning materials in three dimensions. This review focuses on writing techniques that allow construction of three-dimensional

ISSN:1369 7021 © Elsevier Ltd 2004

structures with self-supporting features at resolutions ranging from ~250 μm to 0.10 μm.

Ink-writing techniques

Ink-writing techniques[3,11-30] rely on the deposition of colloid-, nanoparticle-, or organic-based inks to create structures layer-by-layer, as highlighted in Table 1. Three-dimensional ink-writing techniques can be divided into two approaches: (1) droplet-based or (2) continuous (filamentary) inks (Fig. 1). Three-dimensional periodic structures offer the greatest challenge for designing inks, because they contain self-supporting (or spanning) features. Inks are typically formulated from colloidal, polymeric, or polyelectrolyte building blocks[32] suspended or dissolved in a liquid or heated to create a stable, homogeneous ink with the desired and reproducible rheological (or flow) behavior. The important rheological parameters for a given ink design include its apparent viscosity, yield stress under shear and compression, and viscoelastic properties (i.e. the shear loss and elastic moduli), which are tailored for the specific direct-write technique of interest.

Three-dimensional printing (3DP)[19], direct ink-jet printing[22-24], and related approaches such as hot-melt printing[25], involve patterning materials using an ink-jet print head, similar to those used in desktop document printing. These approaches require either low viscosity fluids that must be removed by absorption and evaporation or wax-based inks that are heated during droplet formation and then solidify upon impact cooling. Cima and Sachs[19] pioneered the concept of using ink-jet printing (3DP) to assemble materials. In 3DP, low viscosity binder droplets are printed onto a powder bed to locally 'fuse' material together in a desired pattern. After defining a given two-dimensional layer, an additional powder layer is spread across the bed surface and subsequently patterned. In other ink-jet approaches, three-dimensional structures, such as high-aspect ratio walls or

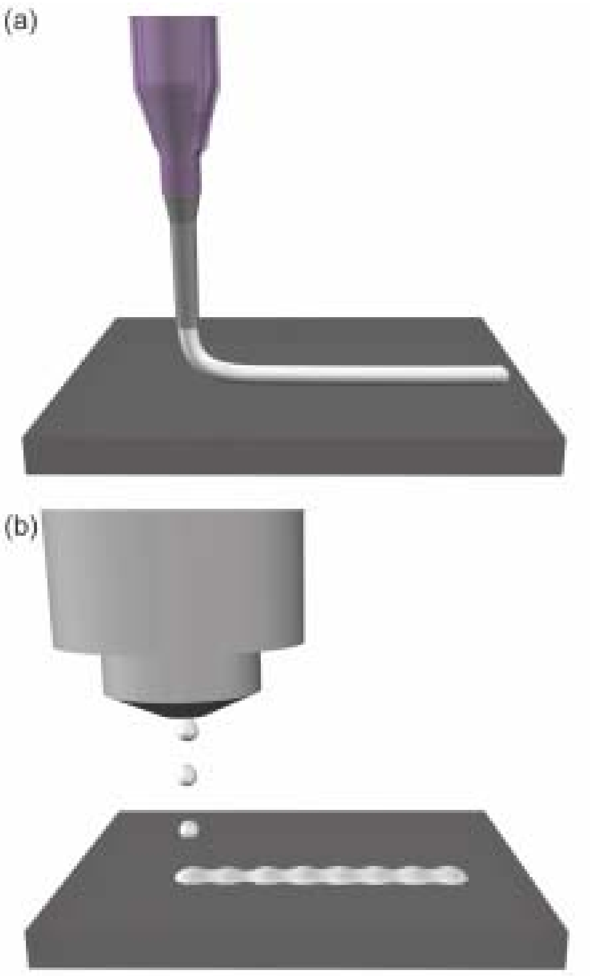

Fig. 1 Schematic view of ink-based deposition schemes: (a) droplet jetting and (b) continuous filament writing. (Reprinted from[31]. ©2002 with permission from Elsevier Ltd.)

Table 1 *Capabilities of ink-writing techniques.*

Technique	Ink design	Minimum printed feature size	3-D periodic structures
Robotic Deposition[11]	Concentrated colloidal gel[13,14]	200 μm diameter	Yes
"	Concentrated nanoparticle gel[15]	100 μm diameter	Yes
"	Viscous polymer solution[16-18]	200 μm diameter	Yes
"	Concentrated polyelectrolyte complexes[3]	<1 μm	Yes
Three-dimensional printing[19]	Binder solution printed on powder bed	170 μm lateral, 45 μm depth	Yes
Ink-jet printing[20]	Dilute fluid[21]	20 μm lateral, 100 nm height	No
"	Concentrated fluid (max. solids ~40%)[22-25]	70 μm lateral, <1 μm height	No
Fused deposition	Thermoplastic polymer melt[26]	100 μm diameter	Yes
"	Particle-filled polymer melt[27] (max. solids ~50%)	100 μm diameter	Yes
Micropen writing[28]	Concentrated, shear-thinning colloidal fluid	25 μm diameter	No
Dip-pen nanolithography[29]	Dilute fluid	20 nm	No
Scanning probe contact printing[30]	Dilute fluid	<500 nm	No

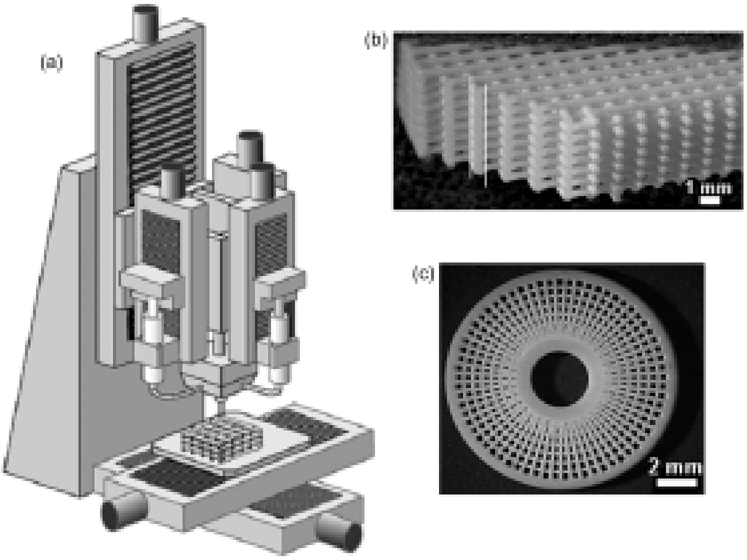

Fig. 2 (a) Schematic of robotic deposition apparatus; (b) optical image of three-dimensional periodic lattice with a simple tetragonal geometry; and (c) optical image of three-dimensional radial array assembled by robotic deposition (nozzle diameter = 200 μm, deposition speed = 6 mm/s) of a concentrated colloidal gel-based ink. (Reprinted with permission from[13]. © 2002 American Chemical Society.)

solid structures, are printed by sequentially depositing inks onto a substrate.

The fluid dynamics involved in drop formation, wetting, and spreading play an important, and also limiting, role in defining the surface roughness and minimum size of the features deposited by ink-jet printing. For example, colloid inks used in direct ink-jet printing[22-24] of ceramics are dilute fluids (maximum solids ~5% by volume). These low viscosity fluids are capable of flowing through the print-head nozzle without clogging and forming consistent drops that solidify by liquid evaporation. Evans *et al.*[23] have shown that ink droplets (initial diameter ~60 μm) produced from dilute colloidal fluids spread on contact with the underlying substrate to a final diameter of roughly 600 μm and a height of ~1 μm or less. While this may be advantageous for assembling thin multilayer structures, it poses severe challenges for other component designs, including those that require self-supporting inks. 3DP is the only ink-jet approach capable of producing such structures, since the underlying powder bed serves to 'support' the printed spanning features. Unfortunately, because of the initial droplet size and the propensity of droplets to spread both laterally and vertically within the powder bed, the printed structures have minimum feature sizes well above 100 μm.

Robotic deposition techniques[11-13] offer new opportunities for three-dimensional patterning of materials at finer length scales. Unlike droplet-based methods, these techniques rely on direct writing of a continuous ink filament in a layer-by-layer build sequence. Lewis and coworkers recently developed several inks, including highly concentrated colloidal[14], nanoparticle[15], fugitive organic[8], and polyelectrolyte[3] inks, capable of direct writing complex three-dimensional structures with minimum feature sizes ranging from hundreds of microns to the submicron scale. In this approach, inks are extruded through a fine cylindrical nozzle (or orifice) to create a filamentary element that is patterned layer-by-layer. By controlling ink rheology, three-dimensional structures that consist of continuous solids[33] and high aspect ratio (e.g. parallel walls)[34] or spanning features[13,14] can be constructed.

Smay *et al.*[13,14] have produced three-dimensional periodic lattices and radial arrays via robotic deposition of concentrated colloidal gels, as shown in Fig. 2. Both the patterned materials and pore channels are interconnected in all three dimensions. Colloidal gels are excellent candidate inks for building such structures, because their viscoelastic properties can be tailored over many orders of magnitude to facilitate flow through nozzles and produce patterned filaments that maintain their shape, even as they span gaps in the underlying layers of the printed structure. While colloidal gel-based inks have many merits, they require significant applied pressures to induce flow during deposition and suffer clogging problems when the nozzle-to-particle diameter ($D/2a$) is reduced to below ~100. We can produce three-dimensional structures with finer feature sizes using

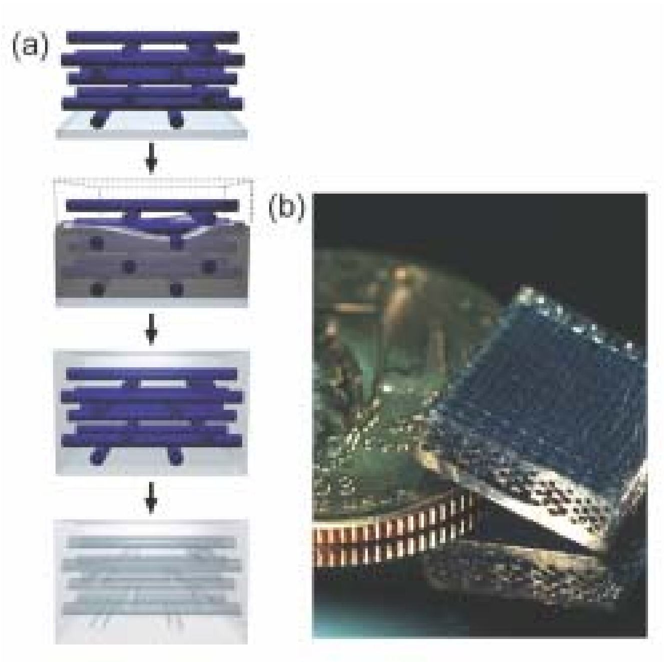

Fig. 3 (a) Schematic of microvascular network assembly and (b) optical image of three-dimensional microvascular network (16-layer structure with interconnected 200 µm cylindrical microchannels). (Reproduced with permission from[8]. © 2003 Nature Publishing Group.)

concentrated nanoparticle inks; however, clogging issues still arise when $D/2a \sim 150$, where D is the finest nozzle used (30 µm in diameter) and a is the radius of largest ink particles[15]. These three-dimensional mesoscale structures may find potential application as tissue engineering scaffolds, if constructed from a bioactive ceramic material[35-37] (e.g. hydroxyapatite), or as structural[38] or functional[39] composites, if the pore space is filled with a second phase.

Therriault *et al.*[8] have produced three-dimensional microvascular networks by robotic deposition of fugitive organic inks, as shown in Fig. 3. First, three-dimensional scaffolds are created by patterning the ink in a layer-by-layer build sequence. The interstitial pore space between patterned features is infiltrated with a low viscosity epoxy. Upon curing, the ink-based scaffold is removed by heating the structure to a modest temperature (~60°C) under a soft vacuum to yield a three-dimensional microvascular network comprised of interconnected microchannels (~100-250 µm in diameter). With the proper ink design, three-dimensional structures comprised of several layers can be constructed, as shown in Fig. 3b. Such structures may have potential for microfluidic systems being developed for a broad range of technological applications, including biotechnology[40], fluidic-based computers[41], sensors[42], chemical reactors[43], and autonomic materials[44].

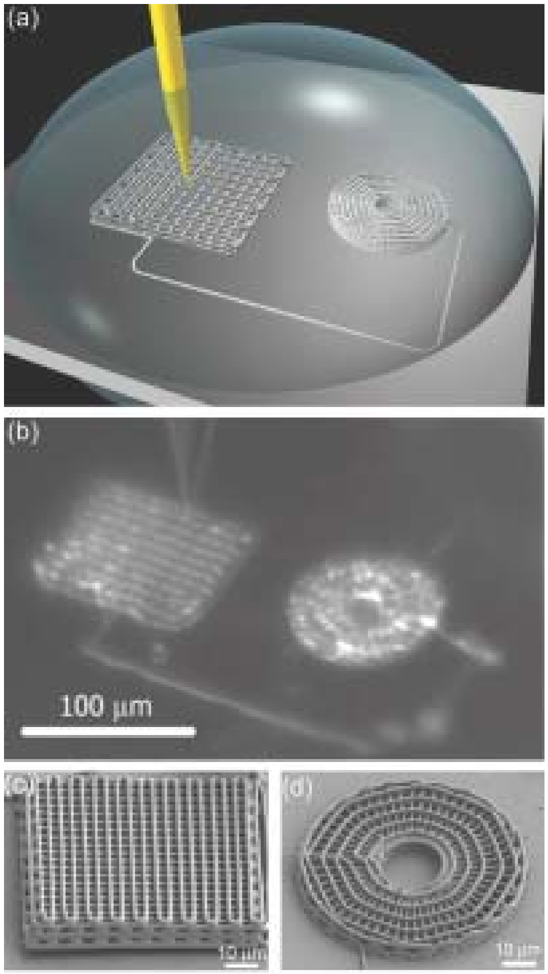

Fig. 4 (a) Schematic of the ink deposition process (not drawn to scale). A concentrated polyelectrolyte ink is housed in the syringe (shown in yellow) immersed in a coagulation reservoir (gray hemispherical drop) and deposited onto a glass substrate (shown in light gray). (b) Optical image acquired in situ during robotic deposition reveals the actual features illustrated in (a), including the deposition nozzle (diameter = 1 µm) that is currently patterning a three-dimensional lattice, and an image of a completed three-dimensional radial array alongside this structure. This image is blurred because the features reside within the coagulation reservoir. (c) Three-dimensional periodic structure with a face-centered tetragonal geometry (filament diameter = 1 µm, ten layers). (d) Three-dimensional radial array (filament diameter = 1 µm, five layers). (Adapted from[3] with permission. © 2004 Nature Publishing Group.)

Gratson *et al.*[3] recently demonstrated the direct-write assembly of three-dimensional microperiodic structures using fluid inks that readily flow through microscale deposition nozzles (~1 µm in diameter or less) and rapidly solidify in a coagulation reservoir (Fig. 4). Fluid inks are well suited to flow through finer nozzles, but must rely on careful matching of coagulation kinetics to the deposition rate to develop the elastic properties necessary for maintaining the desired filamentary shape. This novel ink design uses concentrated, nonstoichiometric mixtures[45] of polyanions and polycations to create the desired initial ink rheology. By regulating the ratio of anionic to cationic groups and combining these species under solution conditions that promote polyelectrolyte exchange reactions[46], homogeneous fluids (40-50 wt.% polyelectrolyte in aqueous solution) are produced with the requisite viscosity for deposition through micro-capillary nozzles of varying diameter (D = 0.5 µm to 5.0 µm). These concentrated polyelectrolyte inks rapidly coagulate to yield self-supporting filaments (or rods) upon deposition into an alcohol/water coagulation reservoir (Fig. 4). The exact coagulation mechanism, driven by electrostatics in water-rich or solvent-quality effects in alcohol-rich reservoirs, and the magnitude of ink elasticity depend strongly upon reservoir composition. Under appropriate conditions, the deposited ink filament is elastic enough to promote shape retention, while maintaining sufficient flexibility for continuous flow and adherence to the substrate and underlying patterned layers. Representative three-dimensional microperiodic lattices and radial arrays assembled by direct writing are shown in Figs. 3c and 3d. These structures can exhibit solid or porous walls, spanning (rod-like) filaments, and tight or broad angled features, revealing the flexibility of the approach. Several polyelectrolyte inks based on mixtures of biologically, electrically, or optically active polyelectrolytes could be developed to allow the assembly of microscale three-dimensional structures of arbitrary design and functionality for applications ranging from photonics to tissue engineering.

Laser-writing techniques

Laser writing techniques[1,2,47-57] create patterned materials through ablation, selective sintering, or reactive chemical processes (Table 2). Each approach places different demands on the laser writing tools and the physico-chemical properties of the material being patterned. Currently, ultraviolet, nanosecond pulsed, excimer, and Nd:YAG lasers are most commonly used, but shorter pulse lasers, such as picosecond and femtosecond lasers, are also finding application as precision writing tools. With the exception of ablative approaches, laser writing is capable of generating complex three-dimensional structures with self-supporting features at resolutions comparable to those achieved by various ink-based techniques.

Ablative techniques involve either directly removing or depositing material. Laser machining is a material removal process, where the substrate to be patterned is exposed to laser energy that ablates off material in specified areas until the desired features are written. Mazumder and coworkers[47] recently reported the direct-write fabrication of multilayer microchannels (minimum channel diameter ~125 µm) in Si via laser ablation, as shown in Fig. 5. Other researchers[48] have used a similar approach for patterning ceramics, which are among the hardest known materials. Alternatively, matrix-assisted, pulsed laser evaporation (MAPLE) creates patterns via materials deposition. This approach, developed by Chrisey and coworkers[49], uses a laser to ablate material selectively from a coated ribbon. The coating contains the material of interest embedded within a thermoplastic polymer matrix. As a pulsed laser scans across the coating-ribbon interface, exposed areas absorb laser energy, undergo pyrolysis, and are propelled toward a flat substrate placed in close proximity to the ribbon. This technique has been used to deposit a wide variety of materials, including metallic, ceramic, polymeric, and even biological materials[50]. However, analogous to hot-melt ink-jet printing, MAPLE is limited to

Table 2 *Capabilities of laser-writing techniques.*

Technique	Laser use	Minimum printed feature size	3-D periodic structures
Laser ablation[47,48]	Removes material in defined pattern	400 nm	No
MAPLE direct-write[49,50]	Transfers material from coated ribbon to substrate	40 µm lateral, 10 nm height	No
Selective laser sintering[51-53]	Locally sinters powder bed	100 µm	No
Laser chemical vapor deposition[54]	Reactive deposition from gas phase induced by local heating at laser focus	10 µm	Yes
Stereolithography[55,56]	Photopolymerization of UV-curable resin at surface	~1 µm	Yes
Two-photon polymerization[1,57]	Photopolymerization of UV-curable resin at laser focus within matrix	120 nm	Yes
Holographic lithography[2,63]	Four noncoplanar beams generate periodic interference pattern in photopolymerizable matrix	250 nm	Yes

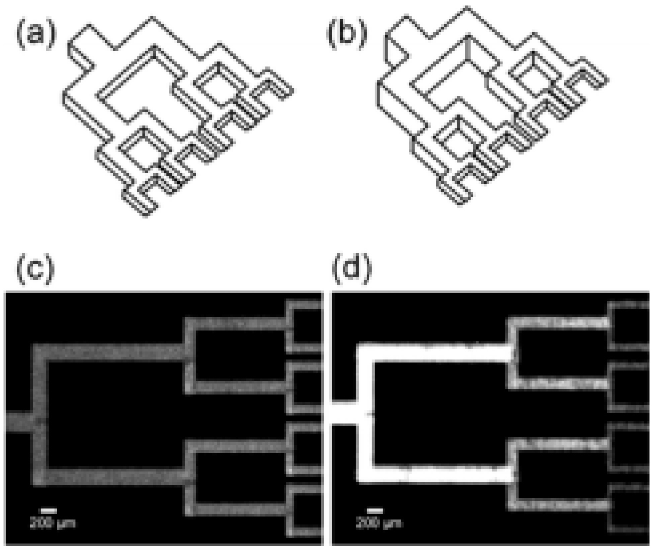

Fig. 5 (a) Schematic of a laser micromachined artificial vasculature system (flat channel, widths of 250, 200, 160, and 125 µm; uniform depth of 125 µm). (b) Schematic of a multidepth channel (widths and depths are equal and are 250, 200, 160, and 125 µm). (c) Image showing intensity levels corresponding to flat channel (a). (d) Image showing the difference in intensity levels corresponding to different channel depths (b). (Reproduced from[47] by permission of The Royal Society of Chemistry.)

patterning two-dimensional layers or simple three-dimensional structures, since the impinging molten material requires an underlying substrate to provide support.

Selective laser sintering (SLS) creates three-dimensionally patterned materials by locally fusing polymer powder through laser writing[51-53]. This approach was invented by Deckard[51] and developed by Bourell *et al.*[52]. It shares a common feature with 3DP in that a layer of powder is spread on a piston and selected regions are bonded together. But where 3DP relies on binder deposition, SLS induces the desired powder adhesion by melting (or viscous sintering). Metals, ceramics, glasses, and polymers can be incorporated into the powder system, but a thermoplastic polymer is needed to bind the materials together. The powder size and melting process limit SLS to structures with feature sizes of ~100 µm or larger.

Laser-writing techniques, such as two-photon polymerization (TPP)[1,57], laser chemical vapor deposition[54], and stereolithography[55,56] rely on reactive chemical patterning of polymeric, gaseous, or liquid precursors. Of these, TPP offers the most promise for creating complex three-dimensional structures at fine length scales (≤1 µm). In the TPP technique, the focus of an intense laser beam is translated within a photopolymerizable matrix (Fig. 6), which is locally cross-linked through the excitation of a two-photon-initiator. Under tight focusing conditions, this writing process creates solidified volume elements (or voxels) of order λ^3 (where λ is the laser wavelength). Kawata *et al.*[57] have achieved spatial resolutions of 120 nm using TPP. Perry, Marder, and coworkers[1] have created several complex three-dimensional structures, including microperiodic structures, tapered waveguides, and cantilever arrays, as shown in Fig. 7. They have also created truly self-supporting three-dimensional structures in the form of cantilevers and microchains[58] (Fig. 7e) that are impossible to replicate by ink-writing or other laser-based techniques, e.g. holographic lithography. In addition, they have demonstrated direct laser writing of Ag, Cu, and Au metallic features, including three-dimensional periodic structures, by two-photon reduction of metal salt precursors and metal nanoparticle growth in

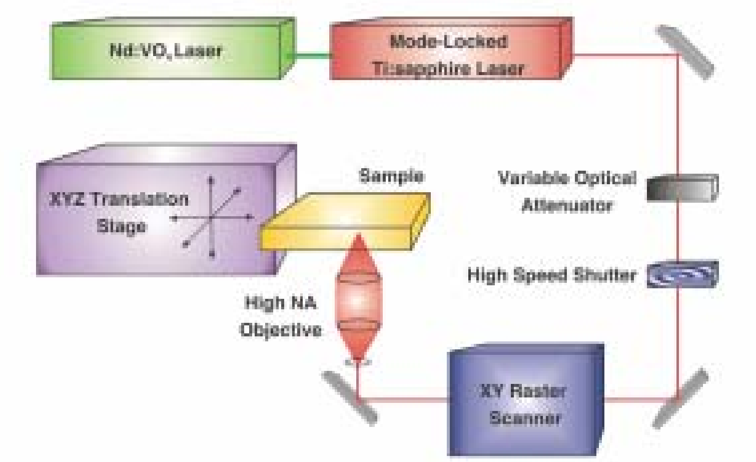

Fig. 6 Schematic of laser writing via TPP. The laser is focused into the sample, which is translated in three dimensions to form the structure. (© 2004 Joe Perry, Georgia Institute of Technology.)

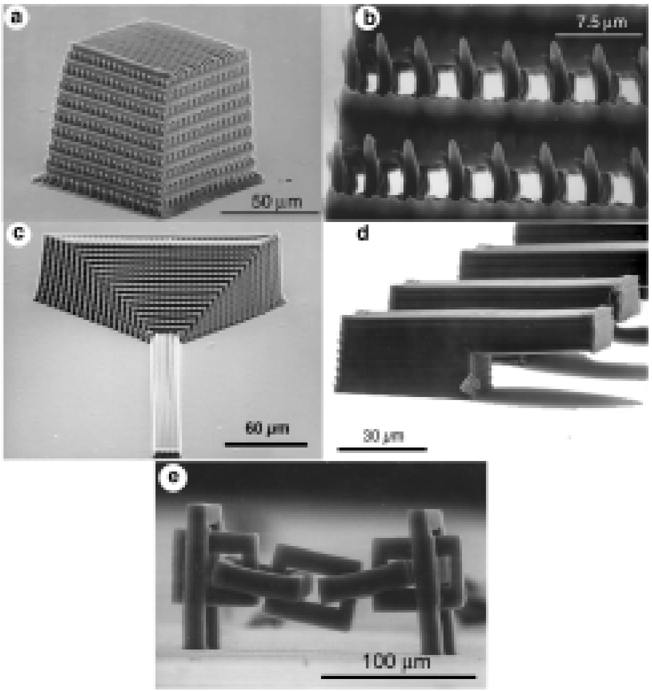

Fig. 7 Images of structures fabricated via TPP: (a) photonic band gap structure; (b) magnified top-view of structure in (a); (c) tapered waveguide structure; (d) array of cantilevers; (e) microchain. (Parts a-d adapted from[1] with permission. © 1999 Nature Publishing Group. Part e reproduced with permission from[58].)

polymer composites[59]. In collaboration with Ober, they have developed efficient two-photon acid generators and applied them to the fabrication of buried microchannel arrays in a chemically amplified positive resist, as well as to TPP of epoxide resins[60,61]. Finally, Braun and coworkers[62] have recently demonstrated that TPP can be used to pattern embedded features (e.g. waveguiding elements) within colloidal crystals whose interstitial pore space is filled with a photopolymerizable matrix. This latter example illustrates the power of combining self- and directed-assembly approaches for advanced materials fabrication.

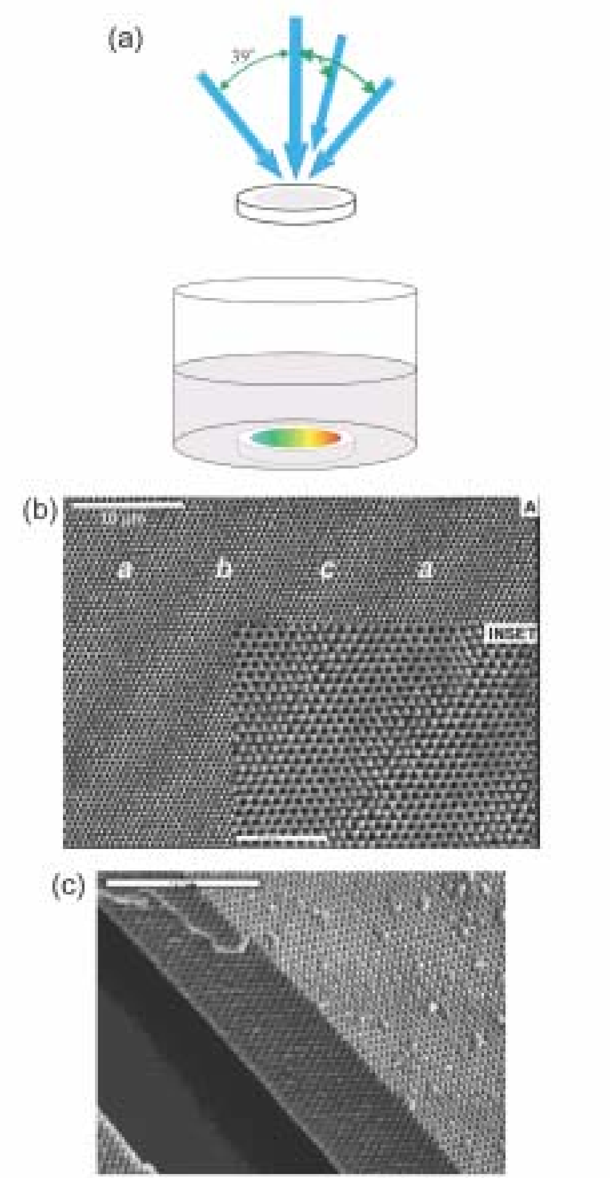

Fig. 8 (a) Schematic of holographic lithography of three-dimensional periodic structures. Blue arrows represent four noncoplanar laser beams. (b) Scanning electron micrograph of the top surface of a patterned silica-acrylate composite showing the abca banding of (111) planes. (c) Cleavage plane of structure in (a). (Reprinted in part with permission from[63]. © 2003 American Chemical Society.)

Opportunities and challenges

Looking toward the future, there are many opportunities and challenges for ink- and laser-writing techniques. Further advances in ink-based writing techniques require new ink designs, better modeling of ink dynamics during deposition, and enhanced robotic and control systems that would allow three-dimensional patterning at nanoscale resolution (≤100 nm). Laser-writing techniques, particularly TPP, are capable of patterning materials with minimum feature sizes approaching 100 nm. However, new multiphoton initiators and matrix chemistries are needed to advance this approach beyond polymeric matrices. Recent efforts by Denning and coworkers[63] have demonstrated that organosils can be pattered into three-dimensional periodic arrays by holographic lithography, as shown in Fig. 8. Holographic lithography cannot be classified as a true direct-write technique because the laser tools are fixed in space. While this is advantageous with respect to fabrication speed, holographic lithography lacks the inherent flexibility of writing patterned features sequentially. Finally, if three-dimensional ink and laser direct-writing approaches are to move from prototyping to larger-scale production, they would benefit greatly by implementing multiple print heads, a concept being pursued in two-dimensional writing techniques, such as dip-pen nanolithography[64], which allows the simultaneous creation of several parts using a given printing platform.

Summary

The direct-write techniques highlighted here offer the ability to pattern materials rapidly in complex three-dimensional architectures over multiple length scales. There is a continual drive toward the development of new writing approaches at finer length scales, which are suitable for a broader array of materials. Given their rapid development, direct-write techniques appear poised to deliver the next generation of designer materials for a wide range of technological applications. MT

Acknowledgments

The Lewis group has benefited from several fruitful collaborations in this area, and wish to specifically acknowledge the contributions of J. Cesarano III (Sandia National Laboratory), J. Smay (Oklahoma State University), and S. White, A. Alleyne, P. Ferreira, and N. Sottos (University of Illinois). The authors gratefully acknowledge the generous support for our work on direct-write assembly through the National Science Foundation (Grant #00-99360 and #01-177792), US Department of Energy through the Frederick Seitz Materials Research Laboratory (Grant #DEFG02-91ER45439), NASA (Grant #NAG8-1922), and the Army Research Office through the MURI program (Grant #DAAD19-03-1-0227).

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