Direct-write assembly of ceramics from colloidal inks

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Abstract

Direct-write assembly of ceramic materials from colloidal inks allows the creation of complex 3-D structures that are inaccessible by traditional processing routes. The success of these emerging techniques hinges critically on the development of colloidal inks with tailored properties. Recent advances in this field are reviewed, which give rise to questions of practical as well as fundamental importance and a broad array of research opportunities.

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1. Introduction

Direct-write assembly techniques [*1,2] offer the ability to design and rapidly fabricate ceramic materials with complex 3-D structures required for structural [3,4], electrical [5–7], photonic [8–10], and biomaterial [11] applications. The techniques of interest involve materials assembly through a layer-by-layer deposition of colloid-based inks. Several techniques are currently under development, including direct ink-jet printing [12], hot-melt printing [*13], micropen [14], and robotic deposition (or robocasting) [15,16,*17]. This nascent area is part of a growing field known as solid freeform fabrication [*18] that provides an enabling technology for forming materials without the use of expensive tooling, dies, or molds.

Direct-write techniques rely on the formulation of suitable colloidal inks for a given deposition scheme. The term ‘colloid’ is used to describe particles that possess at least one dimension in the size range \(10^{-7}\) to 1 \(\mu\)m. A distinguishing feature of all colloidal systems is that the contact area between particles and the dispersing medium is large. As a result, interparticle forces strongly influence suspension behavior. Long range van der Waals forces are ubiquitous, and must be balanced by Coulombic, steric, or other repulsive forces to engineer the desired degree of colloidal stability [*1,19]. Dispersed or flocculated colloidal inks (see Fig. 1) can be created with solids volume fraction and rheological behavior that vary over a broad range. The important rheological parameters for a given ink may include its apparent viscosity, yield stress under shear and compression, and viscoelastic properties (i.e., the loss and elastic moduli). Typically, such parameters are tailored for the specific direct-write technique used.

Direct-write techniques involving colloidal ink deposition can be divided into two approaches: (1) droplet-based and (2) continuous (or filamentary) techniques, as illustrated in Fig. 2. Here, recent advances in this field are reviewed with an emphasis on bulk ceramics fabricated by ink-jet printing and three-dimensional (3-D) periodic structures formed by robotic deposition. These latter structures are of interest for a variety of technological applications, including piezoelectric composites [5–7], structural composites [3,4], tissue engineering scaffolds [11], and photonic band gap materials [8–10]. Opportunities and challenges associated with direct-write fabrication of ceramics are highlighted. Finally, the main concepts are put forth are briefly summarized.

2. Droplet-based techniques

Direct ink-jet printing of ceramics [12] and related approaches, such as hot-melt printing [*13], involve direct deposition of colloidal inks to produce the desired 3-D ceramic structure. Such techniques have as their basis, 3-D
printing (3DP)—a pioneering approach developed by Sachs et al. nearly a decade ago [*20]. Each of these
techniques relies on ink-jet printing of material (e.g.,
colloidal ink or binder solution) in a desired pattern via a
layer-by-layer build sequence.

Ink-jet printing is a well established technology with
many applications, including reprographic, microdispensing,
and materials assembly. Conventional inks for reprographic applications include dye- or pigment-based inks
that are formulated using either a low viscosity fluid that
must be removed by absorption and evaporation or a
wax-based system that is heated during droplet formation
and then solidified upon impact cooling. Such inks serve as
models for colloidal inks developed for ink-jet printing
of ceramics.

The fluid dynamics involved in drop formation and
spreading plays an important role in the colloidal ink
design. Ref. [*13] provides a nice overview of these
considerations, the salient features of which are summa-
rized here. Successful drop formation (ejection) occurs
when the ratio $Re/We$ has a value of 1–10:

$$\frac{Re}{We} = \left(\frac{\gamma \rho a}{\eta}\right)^{1/2}$$

where $Re$ is the Reynolds number ($= \nu a \rho / \eta$), $We$ is the
Weber number ($= \nu (a \rho / \gamma)^{1/2}$), $\rho$, $\eta$, $\gamma$ are the ink density,
viscosity, and surface tension, respectively, $a$ is the
characteristic length, and $\nu$ is the velocity. This dimension-
less group expresses the relative importance of inertial,
viscous, and surface tension forces on fluid flow. If this
ratio is too low, then viscous forces are dominant and a
large pressure drop is required for droplet ejection. If this
ratio is too high, then drop formation can be accompanied
by unwanted satellite droplets.

Drop spreading on impact influences the thickness of the
deposited layer and the lateral resolution of materials
produced by ink-jet printing. Drop spreading can be
estimated by

$$\frac{r_{\text{max}}}{r} = \left(\frac{\frac{We^2 + 12}{3(1 - \cos \theta)} + 4We^2/Re^{1/2}}{1/2}\right)$$

where $r_{\text{max}}$ is the maximum drop radius after impact, $r$ is
the initial drop radius, and $\theta$ is the contact angle between
the ink and the substrate. This expression represents an
upper value for $r_{\text{max}}$, because drop spreading is evaluated
in the absence of solidification.

Colloid inks utilized in direct ink-jet printing [12,22,23]
of ceramics are dilute (maximum solids $\sim 5\%$ by volume)
fluids. They have been formulated to have the appropriate
viscosity and surface tension to facilitate consistent drop
formation and to be agglomerate-free to avoid clogging of
the print-head nozzle. Because such inks undergo solidifi-
cation via liquid evaporation, control over their drying is
critical. A high drying rate is desirable to minimize drop
spreading (i.e., to yield good edge definition and shape
retention). Yet, premature drying of the ink within the
nozzle must be suppressed to avoid clogging. Ink droplets
(of characteristic diameter $\sim 60 \mu m$) produced from dilute
colloidal fluids have been shown to spread on contact with
the underlying substrate to a final diameter of roughly 600
$\mu m$ and a height of $\sim 1 \mu m$ or less [*24]. While this may
be advantageous for assembling thin multilayer structures,
it poses severe challenges for many other component
designs.

Hot-melt (or phase-change) printing of wax-based inks
was originally invented to alleviate the need for ink drying
in reprographic applications. This direct-write approach
has recently been explored by Derby and co-workers [*13]
for ceramics fabrication. They have successfully demon-
strated that wax-based colloidal inks ($\phi \sim 0.3$) can used to
produce ceramic structures with high aspect ratio walls
(minimum wall thickness $\sim 100 \mu m$), as shown in Fig. 3. Although more concentrated inks are required to avoid
defect formation during sintering, this approach appears
promising given their preliminary results.

3. Continuous (filament-based) approaches

Robotic deposition techniques such as robocasting
[15,16,*17], fused deposition [6], and micro-pen writing
[14] also involve the direct deposition of colloidal inks to
produce integrated multi-functional, multi-material, electroceramic thick film devices on planar and curvilinear substrates.

The ink flows through the deposition nozzle when a pressure gradient $\Delta P$ is applied along the length and a radially varying shear stress ($\tau_r$) develops:

$$\tau_r = \frac{r\Delta P}{2\ell}$$

where $r$ is the radial position within the nozzle (i.e., $r = 0$ at the center axis and $r = R$ at the nozzle wall). Depending upon the velocity profile and the ink stability, plug or laminar flow may occur within the nozzle [*17].

Several ink designs have been explored to date, including highly shear thinning colloidal suspensions [14–16], colloid-filled organic inks [6], and, most recently, concentrated colloidal gel-based inks [*17]. Most of these inks solidify by liquid evaporation [14–16] or a temperature-induced phase change [6]. Fluid inks are well suited for assembly of space-filling solids, but rely on careful matching of drying or gelation kinetics to the deposition rate for the development of elastic properties necessary to maintain the desired shape. As a result, these inks are often incapable of supporting their own weight during assembly of 3-D periodic structures with spanning features due to their initial fluidity. In contrast, gel-based inks can be carefully tailored to exhibit a solid-like response throughout the deposition process, making them ideally suited for assembly of such structures.

The rheological behavior of colloidal gel-based inks can be altered through changes in the colloid volume fraction and/or colloidal forces without the need for significant polymer additions (>1–3%). Colloidal gels consist of a percolating network of attractive particles capable of transmitting stress above $\phi_{gel}$. When stressed beyond their yield point ($\tau_y$), they exhibit shear thinning flow behavior due to the attrition of particle–particle bonds within the gel, as described by [25]

$$\tau = \tau_y + K\gamma^n$$

where $\tau$ is the shear stress, $n$ is the shear thinning exponent (<1), $K$ is the viscosity parameter, and $\gamma$ is the shear rate. Gel-based inks flow with a three-zone velocity profile within the cylindrical deposition nozzle that consists of an unyielded (gel) core moving at a constant velocity surrounded by a yielded (fluid) shell experiencing laminar flow and a thin slip layer devoid of colloidal particles at the nozzle wall [*17]. Their elastic properties govern shape retention of the as-deposited spanning elements, as shown in Fig. 4. Such properties can be tuned by tailoring the strength of the interparticle attractions according to the scaling relationship [26,*27] given by

$$y = k\left(\frac{\phi}{\phi_{gel}} - 1\right)^x$$

Fig. 2. Schematic illustrations of (a) droplet-based and (b) continuous (filamentary-based) techniques for direct-write fabrication of ceramics. (Images provided by C. Martinez.)
where $\gamma$ is the elastic property of interest (shear yield stress ($\tau_y$) or elastic modulus ($G'$)), $k$ is a constant, and $x$ is the scaling exponent (~2.5). The equilibrium mechanical properties of colloidal gels are governed by two parameters: $\phi$, which is proportional to their bond density, and $\phi_{gel}$, which scales inversely with bond strength. As the interparticle forces are made more attractive, colloidal gels (of constant $\phi$) experience significant increases in their elastic properties [*20,*21,22,23,*24,25,26,*27,28].

Smay et al. [*17] developed a simple expression to relate spanning ability of colloidal gel-based inks to their elastic properties. The minimum ink elasticity required to assemble a given periodic structure can be estimated by

$$G'_{\text{min}} \geq 1.4\gamma s^4 D$$  \hspace{1cm} (6)

where $\gamma$ is the specific weight of the ink ($= 0.25(\rho_{gel} - \rho_{air})g$), $s$ is the reduced span distance ($= L/D$), $L$ is the span distance, $D$ is the rod diameter, and the maximum acceptable rod deflection is taken to be $0.05D$. Additional details of this analysis are provided in Ref. [*17]. Stronger inks must be formulated as the effective ink density, rod diameter, and normalized span distance increase. These parameters are independent of colloid size, polydispersity, and morphology, therefore colloidal inks can be created from a broad array of particulate materials (e.g., ceramic, metallic, and polymeric colloids).

Invoking this design criteria, 3-D periodic lattices and radial arrays have been produced by robotic deposition from inks containing model silica microsphere [28], functional (e.g., lead zirconate titanate (PZT)) [*17], structural (e.g., alumina and mullite) and biocompatible (e.g., hydroxyapatite) colloids suspended in aqueous solution. As an example, Fig. 5 depicts representative images of 3-D periodic lattices produced from PZT inks. Such structures serve as the active element in 3–3 piezoelectric–polymer composites [5]. This example illustrates the great potential of continuous-based, direct-write approaches for engineer-

Fig. 3. Optical images of a ceramic structure fabricated by hot-melt printing of 30 vol% alumina ink at 100 °C: (a) lower magnification (scale bar 1 mm between minor ticks) and (b) higher magnification views. The pore channels are connected in one dimension only. (Images provided courtesy of B. Derby.)

Fig. 4. (a) Schematic illustration of V-shaped test structure and (b,c) height profiles obtained for V-shaped test structures robotically deposited (nozzle diameter 600 µm, deposition speed 6 mm/s) from 47 vol% lead zirconate titanate inks of varying gel strength at 22 °C. [Note: all dimensions given are in units of mm, and the arrow denotes the direction of increasing gel strength.]
ing complex 3-D structures. These structures simply cannot be produced by conventional ceramics forming techniques (e.g., extrusion, injection molding, etc.). Alternate solid free-form fabrication techniques, such as three-dimensional printing \cite{20}, indirect fused deposition \cite{6}, and indirect stereolithography \cite{11}, may be used to create such structures. However, 3DP yields structures with poor surface finish, while indirect methods rely on a lost-mold approach which requires subsequent removal of large quantities of organic material prior to component densification.

4. Opportunities and challenges

Direct-write fabrication techniques offer the ability to rapidly explore compositional, connectivity, and design variations, opening new avenues for optimizing device performance in an integrated approach. We refer to this new paradigm as combinatorial engineering of materials. In both droplet- and continuous-based techniques, e.g. ink-jet printing and robotic deposition, multiple inks can be dispensed simultaneously. Therefore, one can achieve local compositional tailoring on the size scale corresponding to the minimum feature size (\(\sim 100 \mu m\) currently) within the ceramic component. For example, the 3-D periodic structures highlighted in Fig. 5 could be produced with compositional variations along a given rod, between rods in a given layer, or between layers. Furthermore, design variations such as changes in rod diameter, rod spacing, or lattice geometry within a uniformly periodic or superlattice structure could be implemented. If one considers combining two ferroelectric inks of varying composition or a ferroelectric and ferromagnetic ink together in one structure, the range of compositional, design and connectivity variations that could be explored become immense. The beauty of direct-write techniques is that one can rapidly build large sample arrays (or libraries) that systematically incorporate these variations. In short, such techniques enable the next generation of designer materials by marrying the ability to tailor materials chemistry and rapidly iterate device design.

There are several challenges facing future advances in direct-write fabrication of ceramics, including ink design, modeling of ink dynamics during deposition, robotics, and controls. The design of concentrated colloidal inks with suitable rheological properties is an ongoing effort. An emerging area of emphasis is the development of nanoparticle inks (colloid diameter \(<100 \text{ nm}\)) for direct-write fabrication of nanostructured materials, however new challenges arise in formulating nano-inks due to excluded volume effects and enhanced drying stresses. Understanding the dynamics of both fluid- and gel-based colloidal inks during deposition is another key challenge. One must study ink flow in confined geometries to both avoid nozzle clogging and reduce the minimum feature size to \(\sim 10 \mu m\) (or less). As the nozzle diameter decreases, the applied pressure needed to induce ink flow increases and boundary layer effects become more important. Concentrated colloidal inks exhibit deviations from Newtonian flow behavior, e.g. shear thinning flow behavior. Both droplet- and continuous-based techniques would therefore benefit greatly from the development of models that treat viscoelastic systems and address the effects of surface tension and gravity on shape evolution in the limit of reduced feature size. Advances in robotics and controls are also needed to provide improved positional accuracy and resolution, more efficient building algorithms including the ability to deposit on curved surfaces, multimaterial deposition capability, feedback loops to control deposition at corners or
sharp turns, and integrated sensors. Finally, the designer material capabilities afforded by direct-write techniques can only be capitalized upon by overcoming challenges involved in integrating multiple materials. This highlights the growing need for synergistic interactions between researchers with expertise in materials processing and computational modeling. Multiscale modeling could narrow the vast composition, design, and connectivity space available via direct-write fabrication of ceramics making targeted exploration possible.

5. Conclusions

In summary, direct-write assembly of ceramic materials from colloidal inks allows the creation of complex 3-D structures. Recent advances in direct ink-jet printing and robotic deposition were reviewed with an emphasis on fabrication of bulk ceramics and 3-D periodic structures. Although several research challenges lay ahead, direct-write techniques appear poised to deliver the next generation of designer ceramic materials for a wide array of technological applications.

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Papers of particular interest have been highlighted as: * of special interest.  