Review & Perspective on **Sol-gel Technologies for Additive Manufacturing Glass Materials**

Monisha Murthi, Joel F Destino

Creighton University, Department of Chemistry & Biochemistry, 2500 California Plaza, Omaha, Nebraska 68178

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Abstract

The sol-gel method has shown immense potential in materials science and nanotechnology. One of the cornerstone applications of the sol-gel technique includes the fabrication of inorganic glasses and glass-ceramics at relatively low temperatures as an alternative to conventional high-temperature melt-quench techniques. In recent times, glass fabrication with the sol-gel method has extended to additive manufacturing (AM), also referred to as 3D printing. Current sol-gel, glass AM uses solution-based gel compositions to produce three-dimensional glasses through layer-by-layer deposition and/or using photocurable polymer resins. Owing to its significant advantages of being able to fabricate glass components with arbitrary and complex geometry, AM presents a tantalizing opportunity to fabricate functionalized glass materials, increasing the technique's popularity over the past decade. In this review and perspective, recent progress in combining sol-gel synthesis and additive manufacturing technologies used for obtaining inorganic glasses are discussed, specifically highlighting the research carried out in North America, and a prospectus of the field and emerging areas of interest and need is presented.

Keywords Sol-gel, additive manufacturing, 3D printing, glasses

1. Introduction

1.1 Sol-gel technology for glass fabrication

Sol-gel is a wet-chemical technique for material synthesis, that was first discovered in the mid-19th century, but advanced tremendously in the mid-to-late 20th.[1] A sol is a colloidal suspension of solid particles in a liquid whereas the gel is a colloidal solution of a liquid dispersed in a solid.[2] This method has several advantages, including consistent product quality, consistency in particle shape and size, desirable rheological properties, ease of making multi-component materials, affordability without specialized equipment, and low processing temperatures.[3] Sol-gel technology can be used for various material preparation such as thin-film coating, nanoparticle synthesis, fabrication of metal oxides, organic networks, metal-organic frameworks, composites, glasses, and ceramics. [3–7]

Interest in fabricating inorganic glasses using sol-gel technique emerged in the 1960's when Roy [8] developed a new method of obtaining homogeneous glasses from sol-gel route in a wide variety of silicate and aluminosilicate systems subjected to heating at 600 to 1000 ^{o}C. In the decades since this early work, a vast array of inorganic glass materials has been reported. Examples include, conventional glass formers, such as silicate, phosphate, borate glasses, glass-ceramics, and composite materials.[9, 10] In this array, multicomponent oxide glasses using metal alkoxides from the sol-gel process have been reported to use in a wide range of applications, including optics, transparent electronics, photonics etc.[11–13]

The sol-gel method for obtaining various glass material forms have been described extensively and are illustrated in Figure 1.[3, 14–16] Examples shown include the precipitation of glassy, or amorphous oxide sols and nanoparticles or gelation to form a network and remove solvent by supercritical extraction (or other means) to form aerogels.[17, 18] These low-density,

high surface area materials such as nanoparticles and aerogels have found utility in applications including catalysis and chemical separations.[19–22] The sol can also be used to form thin films commonly applied in optical waveguides [23], dielectrics [24], and coating technologies[25], or drawn/spun into fibers used in various biomaterial and catalysis applications[26–28]. From a gel state, xerogels can be obtained upon solvent evaporation, leaving a porous material, and fully dense bulk materials can be formed through consolidation by traditional ceramic processing.[6, 29, 30] The basic processing principles of glass fabrication by 3D printing, or additive manufacturing, closely follow this last route as highlighted in Figure 1.

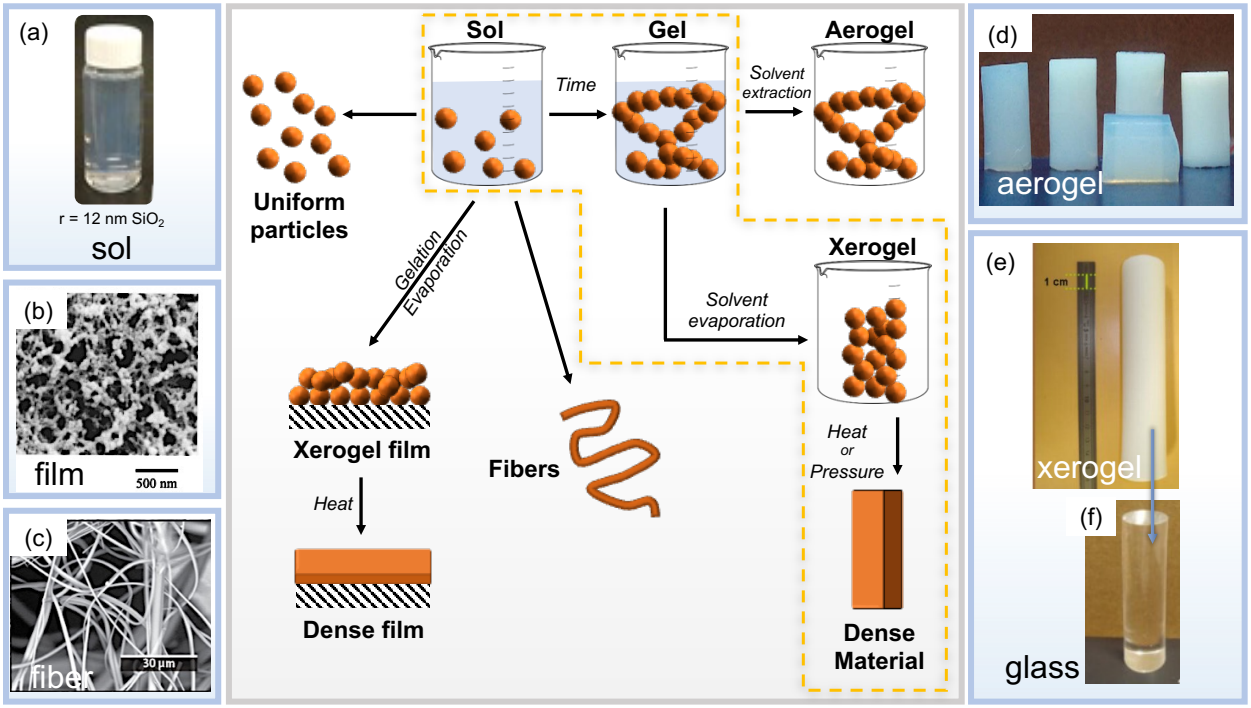

Figure 1. Sol-gel process for materials synthesis and fabrication. (Center) Various routes to different forms of materials. (Left) (a) A photograph from the author's research of a silica sol. Scanning electron micrographs of (b) an amorphous silica xerogel thin film and (c) a composite silica-gelatin fiber. Photographs of a (d) silica aerogel and (e) a silica xerogel and (f) glass. (b) Reproduced with permission from [24], Copyright 1998, Elsevier; (c) Reproduced with permission from [26], Copyright 2017, Springer Nature; (d) Reproduced from [17], under Creative Commons license, 2010, Wiley; (e-f) Reproduced from [29], under Creative Commons license 2011, Optica.

1.2 Additive manufacturing techniques and glass AM overview

Additive manufacturing (AM), popularly known as three-dimensional (3D) printing uses 3D model data for manufacturing objects with precise geometries. In contrast to conventional manufacturing processes like machining, milling, carving, which are inherently subtractive manufacturing methods, removing material to create an object, additive manufacturing provides high precision and saves material wastage, often with a considerable time penalty.[31] In the past four decades, several popular 3D printing techniques have been invented for various applications and material types. Table 1 gives a brief input on the different 3D printing techniques. [32]

Table 1. List of 3D printing technology inventions (chronological order)

3D Printing Technologies	Brief Description	Materials Used	Inventor	Country of Origin	Year
Stereolithography (SLA)	UV resin curing point-by-point	Photopolymer or thermoplastic resin	Chuck Hull	United States	1983
Selective laser sintering (SLS)	Laser-induced sintering	Nylon, polyamide	Carl Deckard and Joe Beaman	United States	1986
Digital light processing (DLP)	UV light resin curing layer-by-layer	Photopolymer-containing resin	Larry Hornbeck	United States	1987
Fusion deposition modeling (FDM)	Thermoplastic filament extrusion	Thermoplastic polymers, polylactic acid	S. Scott Crump	United States	1989
Sheet lamination or laminated object manufacturing (LOM)	Laser cutter layer-by-layer	Paper, polymer, metal	Helisys Inc.	United States	1991
Binder jetting	Precision casting of material and binder	Metal, composites, sand	Emanuel Sachs	United States	1993
Direct metal laser sintering (DMLS) or selective laser melting (SLM)	Laser-induced feedstock melting	Metals (e.g., stainless steel, copper, aluminum)	EOS (Electro Optical Systems)	Germany	1995
Directed energy deposition (DED)	Laser or other energy-source focused coincident with controlled feedstock delivery	Metals (e.g., titanium, steel, copper)	Sandia National Laboratories	United States	1995
Robocasting or direct ink writing (DIW)	Viscoelastic ink extrusion	Polymers, gels, ceramics, metals	Sandia National Laboratories	United States	1996
Two-photon polymerization (TPP) or direct laser writing (DLW)	Laser-induced photocuring of resins point-by-point with high precision	Photopolymer-containing resin	Shoju Maruo, Osamu Nakamura, and Satoshi Kawata	Japan	1997

Electron-beam melting (EBM)	Electron beam melting of material	Stainless steel, polymers, titanium	Arcam AB	Sweden	1997

The 3D printing techniques shown in Table 1 were designed for integrating a diverse range of materials as feedstocks, including polymers, metals, and ceramic powders, nanomaterials, nanocomposites, towards 3D printing a range of plastic [33, 34], metal [35], ceramic [36], and composite structures[37]. Still, inorganic glass AM applications were not reported until well into the 21st century.

The earliest reports of inorganic glass (or simply glass, from here on) 3D printing were direct AM methods, by which conventional bulk glass materials were formed into a melt and rapidly cooled at the point of deposition. In 2015, striking examples of melt-quenched AM soda-lime glass were reported.[38] Here, a molten glass was extruded from the nozzle of a crucible kiln into a thermally controlled chamber to form the glass part. The print feature resolution by this method was relatively large, at approximately 5 cm in diameter. A few alternative AM methods using glass rod feedstocks were demonstrated around the same time. Two approaches using CO_2 laser beams: the first was a powder bed fusion (PBF) method (a broader type of selective laser sintering, or SLS) that directs the laser source at a silica powder bed, and the second was a selective laser melting (SLM) method directing the laser source at a fine glass filament fed through a support.[39] Similarly, a fused deposition modeling (FDM) approach was reported by feeding a borosilicate rod through a heading nozzle onto a substrate.[40] Later, a PBF method was reported for forming porous silica networks with improved resolution and shape control.[41]

The direct methodologies discussed demonstrate early success in glass AM technology for forming complex shapes and structures; however, fabricating glasses without print line prominence and surface defects by these methods is difficult due to thermal gradients, brittleness, and poor

tolerance to process errors.[42] Further, other desirable attributes of AM, such as high-precision processing at the sub-millimeter level and multimaterial fabrication are less accessible, which gave rise to indirect glass AM development.

Indirect glass AM uses molecular or particle-based feedstocks and a multistep process to form a final glass print. In the particle-based feedstock, a slurry, sol or suspension is prepared from a blend of organic solvents and/or polymers and glass-forming (i.e., silica) particles. Whereas in resinous feedstocks, a blend of organic solvents, polymers and liquid molecular or polymeric inorganic precursors are used. Currently, all forms of indirect glass AM require additional treatment to remove organic additives and transform the print into the desired glass component. Typically, post-processing treatments include drying to remove solvents, de-binding to remove polymer and organic contents, and sintering to form the bulk network. Figure 2 categorizes different direct and indirect methods discussed with simplified visual representations.

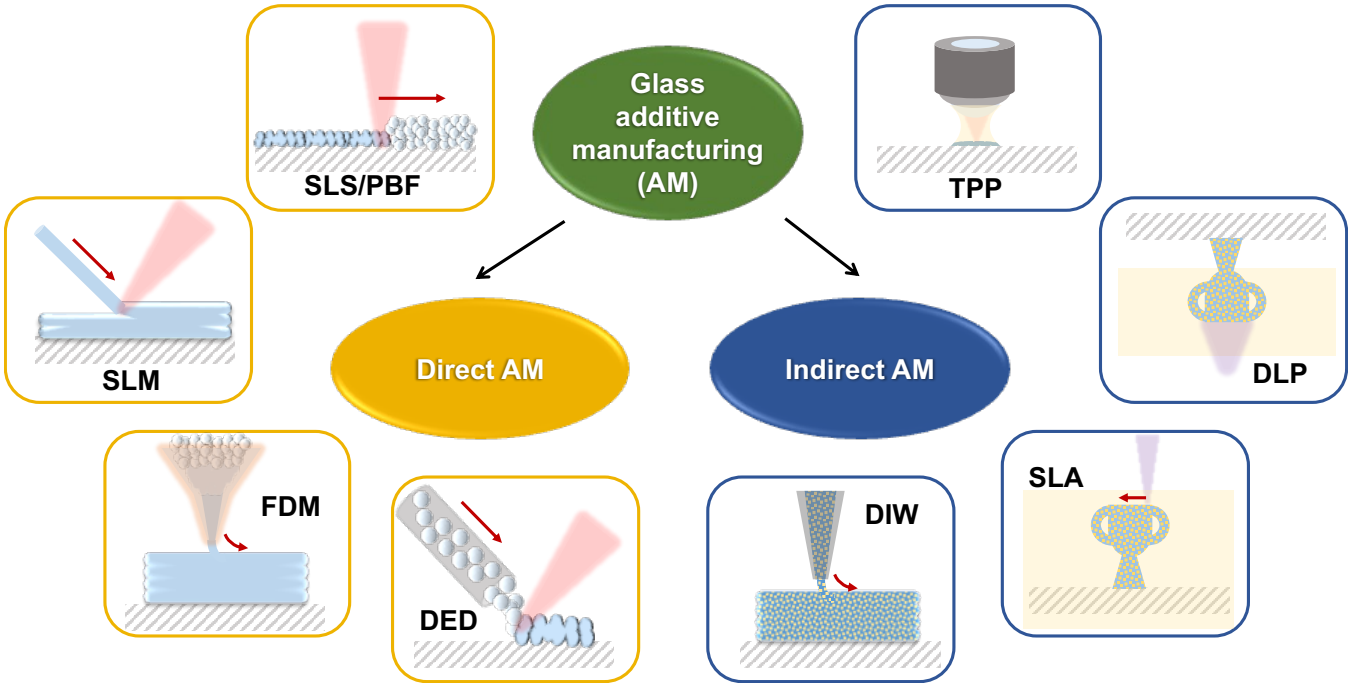

Figure 2. Glass AM categories and examples illustrated for visualization. Direct AM processes involve those where glass part fabrication is obtained in the final form upon printing. Indirect processes involve those where glass additives or precursors (ranging from molecular to particulate) are formed and processed post-printing form the final glass part.

Indirect AM techniques for glass production tend to focus on either sol-gel or particulate-feedstocks and include stereolithography (SLA), digital light processing (DLP), two-photon polymerization (TPP) and direct ink writing (DIW). The first three methods are based on photopolymer resins whereas DIW is traditionally a robocasting or slurry extrusion method. In recent years, several reviews and a textbook have been published detailing the recent advancements in glass AM, writ large.[43–45] Briefly, several types of glass materials have been printed. The earliest report of indirect printing fused silica was an SLA method with a resin composed of a UV-curable photopolymer and commercially available fumed silica (Aerosil OX50).[46] Similarly, at about the same time, a DIW method using fumed silica (CAB-O-SIL EH-5) suspended into low vapor pressure solvent (tetraglyme) was reported. [47]

Several other indirect glass and glass-ceramic printing examples using commercial fumed silica has since been reported, including binary glass networks[48], photoemissive rare earth dopants[49, 50], composites[51], and those that seek to advance printing technology specifications (e.g., resolution) through either unique resin chemistries or AM equipment design[52–57] In bioactive glass (BG) research, a novel 6P53B glass ink was reported from mixing glass particles in a solution.[58] After homogenizing the solution, the glass ink was obtained through a transition from a fluid to gel. These inks were then used for the preparation of glass scaffolds using DIW 3D printing. There also have been DIW, also-called robocasting, approaches using recycled and earth abundant glass materials (i.e., sand).[59, 60] As indirect methods inherently require a conversion from a polymeric, sol, or gel network into the final form (glass, ceramic, composite, etc.), as highlighted in Figure 1, these approaches are readily adapted to the full gamut of sol-gel chemistries.[61] As a result, an in-depth discussion on AM with sol-gel feedstocks for glass and various other materials is presented.

2. Sol-gel feedstocks for AM

The parametric diversity of sol-gel chemistry and processing make them enticing for AM feedstock designers. AM feedstocks are easily accessible over a range of scales, from molecules to macromolecules and colloids through to bulk solids and gels. Figure 3 presents a graphic illustrating the natural synergy between sol-gel synthesis pathways towards forming viable 3D printing precursors for myriad AM technologies.

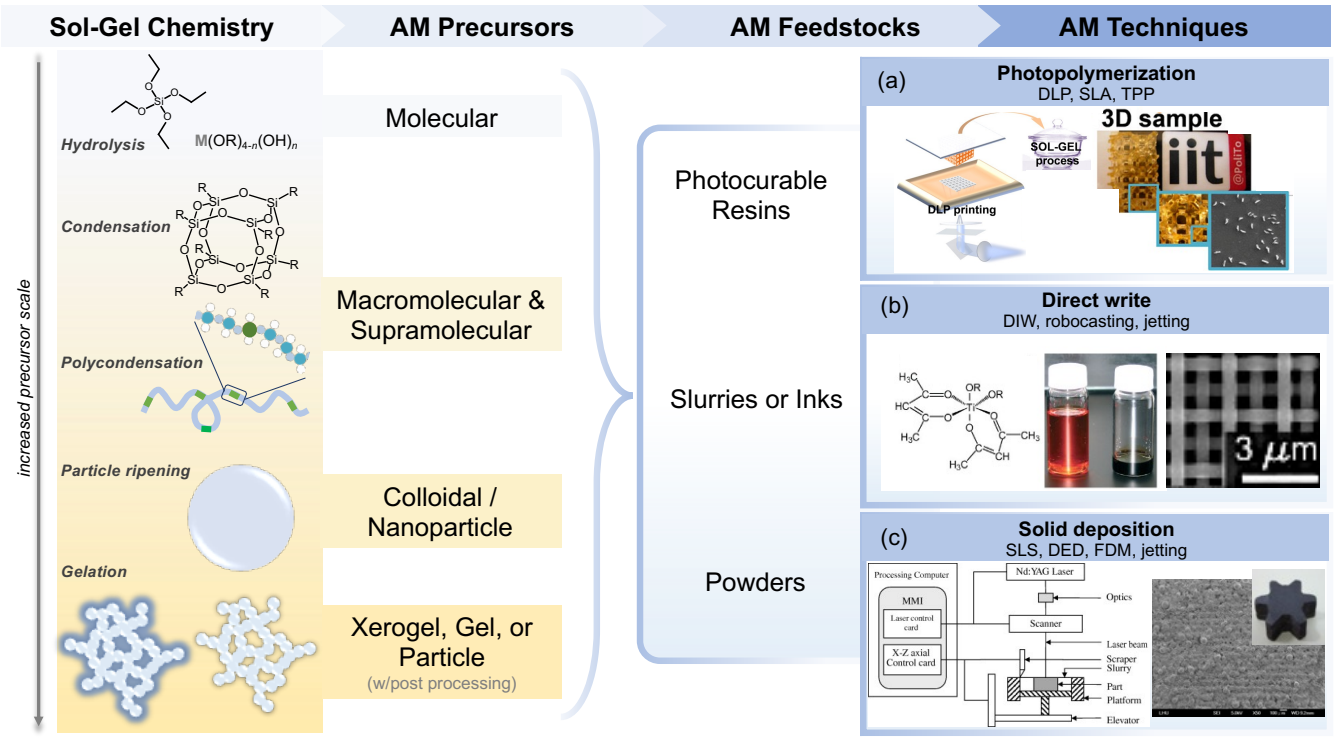

Figure 3. Synergistic relationship between sol-gel chemistry and synthesis of 3D printing, or AM precursors, the resulting AM feedstock type and examples of the various AM technologies for which those materials may be feedstocks, including an example of (a) photopolymerization, (b) direct ink write, and (c) solid deposition. (a) Reproduced with permission [62], Copyright 2016, American Chemical Society; (b) Reproduced with permission [63], Copyright 2007, Wiley; (c) Reproduced with permission [64], Copyright 2011, Elsevier.

Conceptually, as shown in Figure 3, sol-gel chemistry and processing can be tuned to synthesize sol-gel "AM precursors" over a wide range of length scales. Using hydrolytic sol-gel

chemistry as a basis[3], molecular or monomeric AM precursors can be derived directly from alkoxides (shown), salts, and complexes or a hydrolysis product following equation 1.

Hydrolysis: $\mathbf{M}(OR)_4 + nH_2O \rightarrow \mathbf{M}(OR)_{4-n}(OH)_n + n\text{ROH}$ (eqn. 1)

M = alkoxide* central atom

These precursors can be directly formulated into a feedstock material to undergo further processing either during and/or post-print to drive condensation, gelation, and network formation, as given by equations 2-4.

Condensation (i): $\equiv\mathbf{M}\text{-OH} + \text{HO-}\mathbf{M}\equiv \rightarrow \equiv\mathbf{M}\text{-O-}\mathbf{M}\equiv + H_2O$ (eqn. 2)

Condensation (ii): $\equiv\mathbf{M}\text{-OR} + \text{HO-}\mathbf{M}\equiv \rightarrow \equiv\mathbf{M}\text{-O-}\mathbf{M}\equiv + \text{ROH}$ (eqn. 3)

Polycondensation $x(\equiv\mathbf{M}\text{-O-}\mathbf{M}\equiv) \rightarrow (\equiv\mathbf{M}\text{-O-}\mathbf{M}\equiv)_x \rightarrow \mathbf{M}O_y$ (eqn. 4)

Alternatively, condensation and polycondensation chemistry can be controlled to synthesize macromolecular and supramolecular precursors, such as polymers and caged structures, including polyhedral nanomaterials (e.g., silsesquioxanes).[65–67] Varying reaction chemistry, such as pH, water, even introducing sonication or mechanical shear can be leveraged to alter macrostructure and rheology through controlling gelation.[68–71] Further, synthetically tailored colloids or nanoparticles can be obtained under appropriate conditions that favor the formation of stable suspensions to sustain particle ripening.[72–74]

The 3D printing precursors effectively act as finite building blocks that can be formulated into a “AM Feedstocks” either in solution (e.g., a resin for photopolymerization routes, or an ink or slurry with various viscosities) or undergoing a sol-gel transition to form a gel or xerogel that can be further processed into a powder. The AM Feedstocks can then be adapted for use in a range of 3D printing technologies, like those described in the previous section to form gels, composites,

hybrid materials, glasses, or ceramic materials in arbitrary geometries. To best illustrate the types of materials and AM technologies achieved using the described sol-gel AM workflow, a brief review of previous reports is provided.

Ink jetting methods represent one of the most common and oldest additive-based technologies using sol-gel feedstocks. The earliest reports from the 1990s and 2000s focused on 2D printing by either ink jetting or pin-printing low viscosity sols to form patterns and arrays or coating for various ceramics and chemical-sensing applications.[75–79] To obtain a 3D printed structure, methods that control droplet geometry, such as electrohydrodynamic (EHD) jet printing have advanced the field. EHD is an ink jetting method that applies an electric field to a solution containing ions and/or charged particles in a polarizable solvent phase to control droplet shape and addition.[80] This method has shown applications for precise direct writing ceramic and oxide nanowires for electronics fabrication, with nanometer print resolution.[81, 82]

Concurrent with ink jetting advancements, early robocasting technologies laid the groundwork for sol-gel–AM by introducing the use of thixotropic slurry feedstocks comprised of inorganic colloids, a dispersant, and polymeric binders to AM ceramic materials. In this method, stable, shear-thinning slurries were formulated and extruded through a nozzle into printed pre-forms, then treated by conventional ceramics processing.[83, 84] Following this same procedure, in 2007, one of the earliest examples of AM sol-gel feedstocks was reported for fabricating micro-periodic oxide structures by DIW, shown in Figure 3 (b).[63] The ink formulation contained titanium di-isopropoxide bisacetylacetonate (TBDA) as the sol-gel precursor dispersed in polyvinylpyrrolidone (PVP), along with ethanol solvent and the necessary reactants (H_2O and NH_4OH). To prepare the ink, the added alcohol and hydrolysis products were removed by evaporation, yielding a thixotropic, viscoelastic gel amenable for high-resolution (~220 nm feature

size) printing of anatase and rutile titania ceramics. This work paved the way to combining the sol-gel method with different AM techniques to synthesize various new materials.

A method using digital light processing (DLP) to fabricate hybrid nanocomposites was reported which further broadened the field of sol-gel–AM, shown in Figure 3 (a).[62] In this report, the DLP resin contained three main components: (1) tetraethoxysilane (TEOS), undoubtedly the most common sol-gel precursor, to form the silica network; and (2) a methacrylate functionalized organically modified silane (a.k.a., an ORMOSIL) which act as a bridging molecule to join with the (3) diacrylate polymers via photoinitiation and TEOS via condensation. In the end, printed materials with increasing amounts of TEOS were shown to be strengthened by the formation of ~200 nm spherical silica nanoparticles throughout the polymer matrix. However, more broadly, this work had larger implications, as introducing DLP opened the sol-gel–AM space to printing parts with optical systems which would dramatically improve print yield and resolution.

There have been many other noteworthy examples of sol-gel–AM utilizing a wide range technologies for materials applications. To give a very brief summary, organic aerogels formed from resorcinol-formaldehyde and graphene oxide (GO) have been fabricated by DIW for a range of electrical, separation, and catalytic applications.[85] A later example was reported where silica was introduced instead of GO into organic aerogels.[86] Silica and mixed oxide aerogels have also been reported using DIW technology.[87] Laser direct writing has been used to form ceramic, vacancy-rich oxide semiconductors (SnO_2 and ZnO), designed to fabricate 2D gas-sensing devices with high resolution (~ 1 μm).[88] Templated mesoporous silica aerogels have been formed in-situ using DLP and sol-gel chemistry, enabling the production of specialized prints with specific surface areas approaching 400 m^2g^{-1}.[89] In 2020, the DIW of sol-gel titania[63] inspired an in-operando study that better characterized flow properties, shape retention, and microstructural

evolution in the hydrolyzing ink during 3D printing using X-ray spectroscopy.[90] Further, a 3D inorganic ceramic print achieving resolution down to nanoscale (~100 nm) using zirconium-silicon based sol-gel prepolymer (SZ2080) precursor was reported an ultrafast 3D laser nanolithography (3D laser writing) to form polycrystalline ceramics 3D structures.[91]

In all the examples of sol-gel–AM presented, sol-gel chemistry and processing has been key in tailoring the material structure at the molecular and nanoscales, while simultaneously forming micro- and bulk materials for a diverse range of applications, including energy, storage, medical, and environmental remediation.[92, 93] An application where sol-gel–AM has seen much growth is in glass materials.[44, 94] The ability to obtain materials via the sol-gel method and AM glass structures has enabled new functional inorganic glasses with compositionally tailored, high-resolution designer control.

3. Sol-gel–AM for glass material applications

Conventional sol-gel synthesis and processing for glass materials has been well-studied and explored extensively in the last forty years.[3, 14] While facile in a laboratory setting, sol-gel chemistry costs, which can include specialized alkoxides, solvents, and chemical reagents, thermal processing, and waste generation, make the process for manufacturing glass materials at reasonable manufacturing scales prohibitive.[95] AM methods being inherently small-batch and geared towards specialized, designer needs are a natural coupling for sol-gel synthesis.

The earliest forays into glass sol-gel–AM were extensions of previous robocasting/DIW and DLP reports of glass fabrication, which relied on either solid-based, fumed silica particle feedstocks dispersed into organic solvent-based slurries (or inks), and photopolymer-containing resins, respectively.[46, 47] To date, reports have primarily focused on silicates, with a particular interest in optical materials and bioactive glass (BG).

BG is a prime example of a material and application the leverages the advantages of the sol-gel process for tailoring the chemical and physical properties of multicomponent glasses. BG is a soda-lime silica composition that can be formed into a highly porous scaffold material for bone tissue regeneration applications.[94, 96] Silicate glasses are the most widely explored sol-gel-derived BG compositions which was first developed by Hench in 1969 which is then traditionally named 45S5 bioglass.[97] Following this, many other composition BG and glass-ceramics including phosphate, silica-titanate, borate, borosilicate have been extensively researched. Mesoporous bioactive glasses (MBGs) are the latest development of sol-gel derived glasses exhibiting large surface area and porosity. [94]

Being one of the most successful and easily adaptable methods, the sol-gel method is popular for BG manufacture and given the desire to fabricate BG on-demand in unique geometries, they represent a slight majority of publications in this area. A literature review was conducted on sol-gel–AM glasses through available internet sources including Google Scholar, and Scopus, and it was found that nearly 52 % (N =16) of works have been reported on BG, whereas the remaining 48 % (N = 15) were reported on other inorganic glasses. A complete list of sol-gel AM BG manuscripts is included in the Supporting Information, Table S1.

Reports of BG sol-gel–AM extend back more than a decade.[98] In 2011, sol-gel synthesis of a simple binary SiO_2-P_2O_5 by using a one-step sol-gel slurry and DIW was reported.[99] However, most reports have centered on scaffolds made of BG, glass-ceramics and composites, with the use of sol-gel-derived BG powders that are processed *pre*-slurry formulation. Different kinds of sol-gel BG include 13-93 glass[100], 45S5 Bioglass®[101], and MBGs[102] are the most common bioactive materials printed. Sol-gel composites were initially focused on polymer agents that can improve the mechanical properties of the slurry and print, such as polyvinyl alcohol

(PVA)[103], polylactic acid[104], and various bio-sustainable materials, including methyl cellulose.[105]

Several challenges were identified in early efforts to combine BG sol-gel with DIW, namely, their high porosity and specific surface area of BG particles requires large quantities of liquid dispersants, leaching of mobile ions, such as Na^+, that impact particle pH and slurry stability.[106] Around that same time, alternative AM methods were reported, including an example using 58S, a composition of BG that was synthesized by the sol-gel process and prepared a solid-mixture containing nano-glass particles and graphene and fabricated into a scaffold network by SLS.[107] This method did not use a liquid dispersant and reported enhanced mechanical properties attributed to the addition of graphene. In recent years, progress in DIW BG sol-gel–AM has improved and yielded promising in vitro and in vivo studies for future applications in medical intervention.[96, 108] Unfortunately for the scope of this review, much of the 3D printing BG sol-gel research has taken place outside of North America. The lone example is an indirect filament-based AM approach by first forming 45S5 BG by sol-gel microwave synthesis, and then mechanically combining the resulting glass with polylactic acid (PLA).[104]

For pure silica glass sol-gel–AM, a diverse breadth of chemical methodologies has been explored. An early report describes starting from molecular precursors including acidic hydrolysis of (1) TEOS, which served as the silica precursor, (2) APTMS, an acrylate containing ORMOSIL, that served as the polymerizable component, and (3) the addition of ammonium acetate and water to promote condensation in the photocurable sol that was coupled with stereolithography (SLA).[109] The authors demonstrated the formation of gel print forms in unique geometries that could then be thermally processed to form xerogel and fully-dense, transparent, silica glass objects for a range of applications, including miniature chemical glassware. Recently, a multi-component

glass system, including binary (Al_2O_3-SiO_2), ternary (ZnO-Al_2O_3-SiO_2, TiO_2-Al_2O_3-SiO_2), and quaternary oxide (CaO-P_2O_5-Al_2O_3-SiO_2) was reported using DLP.[56] The authors were able to further post-process modify the printed parts, impregnating the nanoporous glass with photo-emissive ions (e.g., Eu^{3+}, Tb^{3+}), nanocrystals ($CsPbBr_2Cl$), and organic emitters (Rhodamine 6G). Beyond these reports, several noteworthy North American efforts have further advanced glass and optics sol-gel–AM and are highlighted at length in the following section.

4. Sol-gel–AM for glass material applications: Highlights from North America

A review of the literature (collected from Google Scholar and Scopus) shows that the use of 3D printing technology for glass materials has grown modestly as seen through the bar graph (Figure 4 (a)) which illustrates the number of articles published across other countries and North America from 2014 till now. Further, in Figure 4 (b) different types of AM techniques adopted for glass prototyping from North America are represented in a pie chart. The pie chart shows that among the different printing techniques, DIW has represented the largest effort, with photopolymerization methods (including SLA, DLP, and TPP), being the second most common.

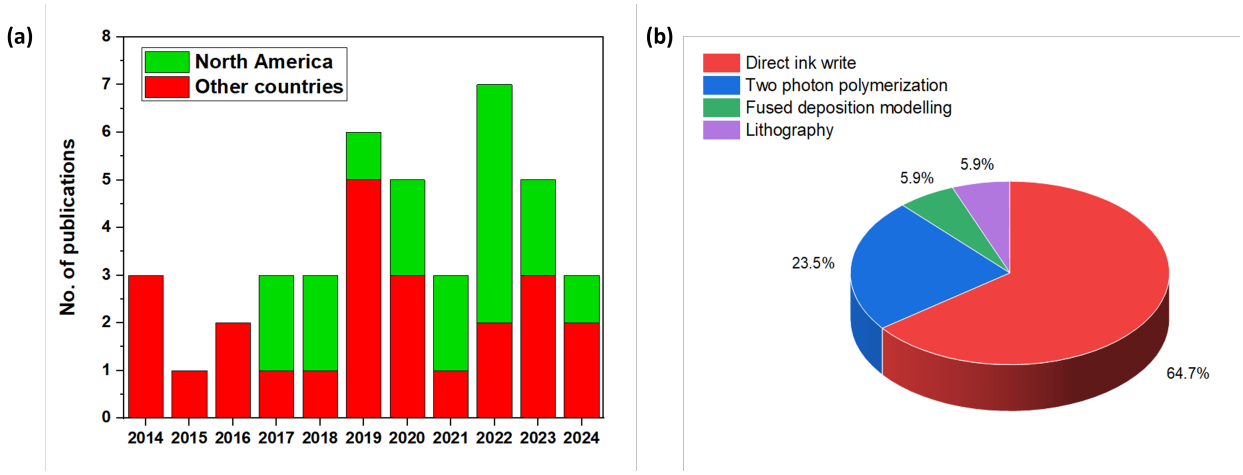

Figure 4. (a) Research glass sol-gel–AM publications from 2014 till now across other countries and North America and (b) 3D pie chart showing different glass sol-gel–AM techniques from North America

Figure 5 presents a visual contextualization of the sol-gel–AM glass progress from North America, containing images and key results from the past seven years. The graphic is divided in half to represent most works, which fall into either direct write or lithography (including photopolymerization methods such as DLP and TPP). As detailed in section 1, sol-gel AM for glass material applications is an indirect method, coupling procedures and technologies previously published using fumed silica [46, 47] with the various sol-gel AM precursors and feedstocks detailed in section 2/Figure 3. A complete list of manuscripts authored on sol-gel–AM for glass material applications from North American can be found in the Supporting Information, Table S2, for easy of review to accompany the discussion.

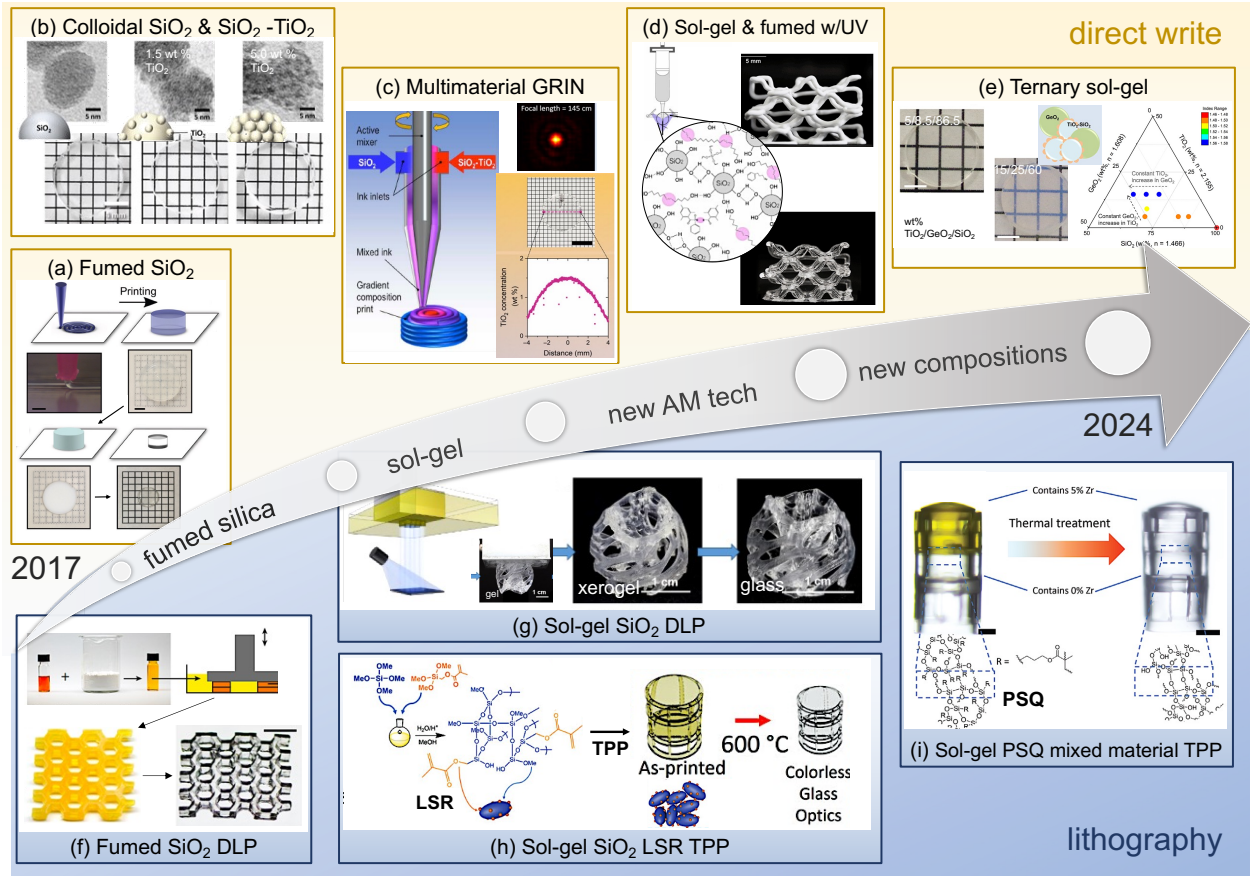

Figure 5. A graphical summary of sol-gel glass AM advances, contextualizing and highlighting work from North America. (a) Reproduced with permission [47], Copyright 2017, Wiley; (b) Reproduced with permission [110], Copyright 2018, Wiley; (c) Reproduced from [111], under Creative Commons license, 2020, American Association

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4.1 DIW

Within North America, there has been significant progress developing DIW glass AM, primarily leveraging the advantages of particulate or colloidal sol-gel precursors to prepare slurry inks for single composition, mixed composition, and multimaterial glass printing. This sol-gel approach mirrors a previously described indirect AM report (Figure 5 (a)) [47]. In the sol-gel version, the glass precursors particles were SiO_2 colloids (~22 nm in diameter) synthesized by the Stöber method[72] from TEOS, and binary raspberry-like SiO_2-TiO_2 colloids between 25-40 nm in diameter were grown with the addition of titanium isopropoxide.[110] A graphic depicting the particles and glass is shown in Figure 5 (b). The resulting inks were conveniently one-pot from particle synthesis to suspension formulation, and were approximately 35 wt % inorganic solids loading. A range of silica and silica-titania glasses (0-8 wt % TiO_2) were reported and characterized. Most notably, this was the first report of optical quality glasses, as compared to melt-quench standard fused silica and ultra-low expansion (or ULE) glasses on several structural, physical, and optical properties. It also demonstrated the ability to tune material composition using sol-gel chemistry.

An international collaboration between three groups, including one in North America, reported an approach combining sol-gel with fumed silica feedstocks in a UV-cured DIW AM method to achieve transparent fused silica glass with improved mechanical properties (Figure 5 (d)).[112] The ink comprised of Aerosil® OX50 and TEOS along with photopolymer (

(hydroxyethyl)methacrylate (HEMA), 2-phenoxyethanol (POE), and tetra (ethylene glycol) diacrylate (TEGDA). The addition of TEOS to the ink was shown to improve the solids loading in the ink (from 40 to 50 wt %), while simultaneously improving shear-thinning behavior, and sintered-glass transparency. The implementation of UV-curing further improved printed-part stiffness, as shown by rheological measurements and printing examples.

The first example for multimaterial glass prints was for silica and silica-titania glasses using a mixed precursor approach. Hydrophilic fumed silica particles were combined with TBDA to create the inks.[48] In this work, fundamental colloid model equations were applied relating elastic modulus to particle charge and size to regulate ink rheology to minimize viscoelastic response differences between inks composed of silica and those of silica-TBDA. Doing so enabled controlled blending of the two inks in-line pre-nozzle to program print compositional profiles and was the first report of a gradient composition glass print. Such incremented advancements ultimately came together demonstrating the power of DIW and glass sol-gel–AM for fabricating conventional and freeform gradient refractive index (GRIN) lenses.[111] Here, as shown in Figure 5 (C), compositional gradient designs were achieved within the print by using the ink formulations described in[110], and varying the concentration of titania which served as the index-modifying dopant, ultimately achieving a refractive index range of 1.46-1.49.

Looking at other glass-former systems, germania-silica glasses were first demonstrated using a mixed particle approach. A dilute sol was prepared by adding a tetraethoxygermane (TEOG) sol to a TEOS sol, in other words, independent GeO_2 and SiO_2 species were mixed. Following a similar one-pot approach to the method described, the ink was obtained, printed by DIW, and then converted to glasses with varying germania concentrations (0-5 wt %).[116] A core-shell germania-silica colloidal was later reported, presenting similar results, with optical

quality transparent DIW glasses up to 6 wt % GeO_2.[117] However, in both methods, compositional inhomogeneity was observed by electron spectroscopy at the microscale, believed to be due diffusivity of Ge in silica at high temperatures [118] and challenges with precursor particle synthetic control, respectively.

The first reported AM ternary glass system was achieved using a mixture of GeO_2 colloids and TiO_2-SiO_2 core-shell feedstocks towards improving the refractive index range (Δn) previously (Figure 5 (e)).[113] A transparent glass composed of 20/15/65 (w/w/w, %) GeO_2-TiO_2-SiO_2 was printed that gave a refractive index of 1.576, which is a Δn of 0.115 in comparison to pure silica glass. Interestingly, the authors found titania had a larger effect on the refractive index, while germania had a larger impact on dispersion. Challenges were noted as increasing concentrations in ternary glasses were limited by the anatase TiO_2 crystallization and phase separation of GeO_2, diminishing optical transmission. Still, this work tremendously improved the achievable Δn with significant implications for AM GRIN optics with tailored index and dispersion profiles. It also demonstrates multi-dimensional, cross-compatibility of amorphous sol-gel colloids for AM glass.

4.2 Photopolymerization/Lithography

Prominent glass AM technologies from North America include photopolymerization strategies utilizing sol-gel-based macromolecular structures in resinous feedstocks. These approaches differ from DIW efforts which generally seek to advance multimaterial capabilities, instead, they primarily focus on single composition glass printing, towards improving print resolution and reducing post-print processing. The earliest example of such was a TPP 3D printing technique combined with a sol-gel resin to achieve transparent glass micro-optics for high-precision applications (Figure 5 (h)).[114] Here, a solvent-free liquid silica resin (LSR) was synthesized by hydrolyzing and pre-condensing an acid-catalyzed tetramethoxysilane (TMOS)

precursor with sub-stoichiometric amounts of water, along with a photocurable crosslinking silane, methacryloxymethyltrimethoxysilane (MMTS). Unlike sol-gel processes that commence from molecular feedstocks, the LSR comprises of macromolecular structures that include a polymerized core with hydrolyzable and organic substituents, minimizing the presence of undesired purely organic products within the resin. Post-printing, the hydrolyzable groups and organic groups cross-link via condensation and UV-curing, respectively, and the parts were thermally processed to form high-density silica structures. This work demonstrated the capability of the method for AM imaging micro-optics, including a lens and spectrometer system orders of magnitude smaller than conventional equivalents.

A similar approach was adapted utilizing polyhedral oligomeric silsesquioxanes (POSS) as silica precursors.[54] Here, a commercially obtained acrylic POSS (polyoctahedral silsesquioxanes, Hybrid Plastics MA0736) was mixed with trifunctional monomer and photoinitiator and used to print micro-optical components by TPP. The report does not identify this work as being sol-gel; however, such POSS solid precursors require stabilization in a sol resin, and the unfunctionalized groups (here, ethoxides) ultimately require hydrolysis and condensation, in addition to the acrylate cross-linkage, undergoing a sol-gel transition and needing additional thermal treatment to render the inorganic glass. Thermogravimetric analysis of the resin shows that the final silica glass component accounts for approximate 35-40 wt % and suggests full density glass is formed under 700 ^{o}C and is “sinterless”.

Adding to the macromolecular approach, the team that reported an LSR, developed a POSS-like feedstock, referred to as a polymeric silsesquioxane (PSQ) resin (Figure 5 (i)).[115] The report touted reduced shrinkage, improved print fidelity, lower temperature processing, and improved moisture stability, a challenge for macromolecular oxo-structures which tend to hydrolyze and gel

with ambient water. The PSQ resin enabled TPP glass print resolution of < 200 nm, and network glass condensation at 650 °C, with increased inorganic loading, at ~ 46.2 wt %. While much of this manuscript is discussed in comparison to [54], another key advancement in this report includes incorporation of a zirconium alkoxide precursor stabilized with methyl acrylic acid to form a TPP Zr-doped silica glass resin. An example of a multimaterial weld print featuring a micro-optic with a base formed from a silica PSQ followed by adjoining lens formed from a 5 % Zr-doped PSQ was shown and characterized in detail.

5. Prospectus and perspective on sol-gel–AM for glass and other materials

The breadth of approaches from North America demonstrates the synergy between sol-gel feedstocks and indirect glass AM, from macromolecular to synthetically tailored colloids or nanoparticles. While the full range of sol-gel–AM combinations are far from realized, the benefits of synthetic control across length scales are undeniable. Despite the immense opportunity, feedstock pairings with AM technologies have been largely siloed. Colloidal sol-gel feedstocks have been preferred in DIW printing, while molecular and macromolecular sol-gel precursors have been preferred in photopolymerization resins. Theoretically, there is no reason that (1) colloidal feedstocks cannot be equally as useful for photopolymerization, so long as they do not interfere with the wavelengths necessary for photocuring; and (2), macromolecular sol-gel precursors can be used for DIW and extrusion-based methods so long as they exhibit thixotropic rheological behavior. Reports described here present examples suggesting the validity of the first ([46, 53]) and second ([112]) points. Research cross-pollinating and intermixing approaches could more rapidly advance the field and yield intriguing new results.

Glass AM reports have primarily focused on silica printing, with emphasis on improving feature resolution using existing feedstock approaches (i.e., fumed silica photopolymer composite

resins, sol-gel precursors, etc.) combined with new AM technologies. The drive to push resolution is fueled by optical applications, and rightfully addresses those needs; however, careful analysis of the published data suggests that only slight material improvements have been realized from the earliest reports. For example, the push for low temperature processing and "sinterless" glasses are on trend, but curiously, thermogravimetric analysis from the earliest reports of sol-gel and fumed-silica glass AM shows similar profiles with complete decomposition of non-glass additives below 700 °C. [46, 110] Without the full complement of key optical silica glass characterization metrics (e.g., hydroxyl content, Q-speciation, porosity/density, and residual organic content, etc.) such claims of network densification are challenging to assess. Efforts to more directly improve inorganic solids loading in sol-gel and other indirect glass AM feedstocks would be more valuable to advance the field. As well as efforts to advance lower-density and hybrid (inorganic-organic) glass AM prints for new applications spaces.

Still, there are new opportunities to integrate sol-gel materials with emerging AM methods. Two promising AM technologies include volumetric additive manufacturing (VAM) and laser powder deposition (LPD). VAM enables rapid prototyping using microscale computed axial lithography (micro-CAL).[119] Parts can be fabricated rapidly by this method without the limitations of slurry viscosity and printed part mechanical strength, which are major issues for building complex geometries by DIW and conventional photopolymerization techniques, respectively. A recent effort to develop fumed silica particle resins demonstrated that precursors with up to 40 vol. % silica solids (the equivalent of ~ 60 wt %) were achievable with only 25 % shrinkage.[120] LDP uses powder jetting in a gas stream to deposit material at a point coincident with a CO_2 laser beam, where particles are either sinter or melt to substrate or other particles.[121] Examples of multimaterial printing for fiber optic applications with silica, alumina, titania, and

erbia powders were demonstrated. Sol-gel materials could be integrated into either technologies for optical glass and ceramic AM, while VAM could be particularly beneficial for hybrid sol-gel applications.

Looking beyond silica, very limited research into glass sol-gel–AM has been presented in the literature, as shown in Table S2. This is likely because of the significance of silica glass in a wide range of technologies, as well as the wealth of research in sol-gel silica chemistry and processing. Pursuing new compositions incurs a significant time investment to advance chemical and physical understanding of the synthetic and processing routes available. The parametric nature of sol-gel has historically been the source of allure to novices, as well as joy and bewilderment for practitioners. Towards that end, materials discovery innovation in the areas of automation, machine learning, and artificial intelligence present new, appealing opportunities for exploring sol-gel AM, as has been shown in other areas of materials science and engineering.[122, 123] Multimaterial AM also presents unique opportunities to interrogate basic materials science and chemistry questions by rapidly generating wide compositional ranges and combinations of materials for characterization and testing.[124, 125]

Beyond glass and ceramics applications, sol-gel has been a cornerstone technology for forming composites, and hybrid organic-inorganic amorphous materials for diverse applications including chemical separations, sensors, and antifouling materials.[6, 126] Much research exists leveraging the controllability of the sol-to-gel transition for thin film and coating applications, as well as two-dimensional printing methods, like ink jetting. However, 3D printing offers an opportunity to hierarchically control material structure and produce multimaterial compositions in ways that have not been explored. Revisiting and integrating AM with sol-gel technologies is likely a fertile space for new research in fabricating novel materials and devices.

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