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REVIEW ARTICLE

3D printing of glass by additive manufacturing techniques: a review

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Abstract Additive manufacturing (AM), which is also known as three-dimensional (3D) printing, uses computer-aided design to build objects layer by layer. Here, we focus on the recent progress in the development of techniques for 3D printing of glass, an important optoelectronic material, including fused deposition modeling, selective laser sintering/melting, stereolithography (SLA) and direct ink writing. We compare these 3D printing methods and analyze their benefits and problems for the manufacturing of functional glass objects. In addition, we discuss the technological principles of 3D glass printing and applications of 3D printed glass objects. This review is finalized by a summary of the current achievements and perspectives for the future development of the 3D glass printing technique.

Keywords three-dimensional (3D) printing, glass, fused deposition modeling (FDM), selective laser sintering/melting (SLS/SLM), stereolithography (SLA), digital light processing (DLP), direct ink write (DIW), optical devices, microfluidic

1 Introduction

Three-dimensional (3D) printing is a technique that uses computer-aided design to build objects layer by layer. This approach differs from traditional manufacturing, which relies on cutting, drilling, and grinding away unwanted excess from a solid piece of material such as metal [1]. In 1986, Hull proposed a stereolithography (SLA) technique, which used ultraviolet (UV) light to cure high-molecular weight polymers and stack them layer by layer [2]. In the same year, he founded the world's first 3D printing company, 3D Systems. After more than 30 years of development, the 3D printing technique is rapidly evolving owing to its advantages of material saving, high production efficiency, and low cost. Currently, 3D printing technologies, such as fused deposition modeling (FDM), SLA, selective laser sintering/melting (SLS/SLM), and digital light processing (DLP) [3–5], have been widely used in various fields including industrial design, sculpture, clothing, automotive, construction, and aerospace [6–10].

Currently, the mainstream materials for 3D printing are metals, resins, plastics, and ceramics [11,12]. While 3D printing of glass materials has been demonstrated on a laboratory-scale, large-scale commercial application remains elusive in the near future. Owing to excellent optical properties, mechanical properties, thermal stability, and electrical/thermal insulation, glass is widely used in our daily life [13,14]. These excellent properties make glass an important material, which is widely used in various fields such as chemistry, biology, and optics [15–18]. The 3D glass printing technique can produce glass components with complex shapes and structures and also offers a novel route for the high-precision processing of glass on the sub-millimeter level, which is difficult to achieve by traditional glass manufacturing techniques. 3D printed glass structures combine customization and high resolution to enable the creation of new functional glass materials.

Here, we review the research progress in the development of technologies for 3D printing of glass. We focus our discussion on the glass materials used for the 3D printing technique, problems associated with 3D printing of glass, and the applications of 3D glass printing technique in the fields of personalized printing, optical components, and microfluidic chips.

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2 Additive manufacturing techniques for glass

2.1 Fused deposition modeling

FDM is an additive manufacturing (AM) technique that is suitable for manufacturing complex parts [19,20]. FDM was invented by a company called Stratasys, which has trademarked the term. Other companies refer to this type of technology as fused filament modeling (FFM) or fused filament fabrication (FFF) [21–25]. The FDM technique for 3D glass printing relies on the use of a computer-controlled heating nozzle which moves along the *x*–*y* plane according to the section profile information of produced parts. During printing, glass is heated to the molten state and piped to the hot melt nozzle, where the molten glass is extruded, selectively coated on the work table and rapidly cooled to form a thin profile. After completing one layer, the table is moved downwards, and the abovementioned process is repeated to print the next glass layer; finally, a 3D product can be produced [26,27]. The temperature-dependent viscosity property of glass is crucial in this technique.

During FDM 3D printing, it is essential to maintain the temperature of the raw material ejected from the nozzle, which is usually higher than the freezing point of the raw material. If the temperature is too high, the accuracy of the printed object will be reduced, and the model will be deformed. If the temperature is too low, the print head will be blocked, and the printing will fail [28,29].

Klein et al. [30] have designed and built a system for printing silica glass. In their approach, the 3D printing nozzle continuously extrudes molten glass at a constant speed. By controlling the movement of the nozzle, they can print different shapes of glass (as shown in Fig. 1). The scanning electron microscopy (SEM) image shows that the printed glass has smooth surface; in addition, the printed glass has high optical transmittance.

Baudet et al. have printed chalcogenide glass objects at much lower temperatures (Figs. 2(a) and 2(b)) [31]. They studied the physicochemical properties of the sample and determined that the chemical and thermal properties were not significantly different from those of the original glass (Figs. 2(c) and 2(d)). More importantly, they demonstrated that 3D printing was an appropriate technique for making complex optical components from chalcogenide glass, including multi-material fiber preforms with geometry and structure that were not achievable by conventional techniques.

In 2015, the additive manufacturing team at the Ningbo Institute of Materials Technique and Engineering, Chinese Academy of Sciences, developed a glass melting deposition molding technique (Fig. 3). In addition, they developed a high-temperature-resistant, high-precision Al_2O_3 ceramic nozzle and tabletop scale printing equipment for the FDM process [32]. Using this system, they successfully printed various micron-scale glass parts with a characteristic size of less than 50 μm and a linear printing speed up to 10 mm/s; the issues of high operating temperature and poor process stability during glass printing were circumvented.

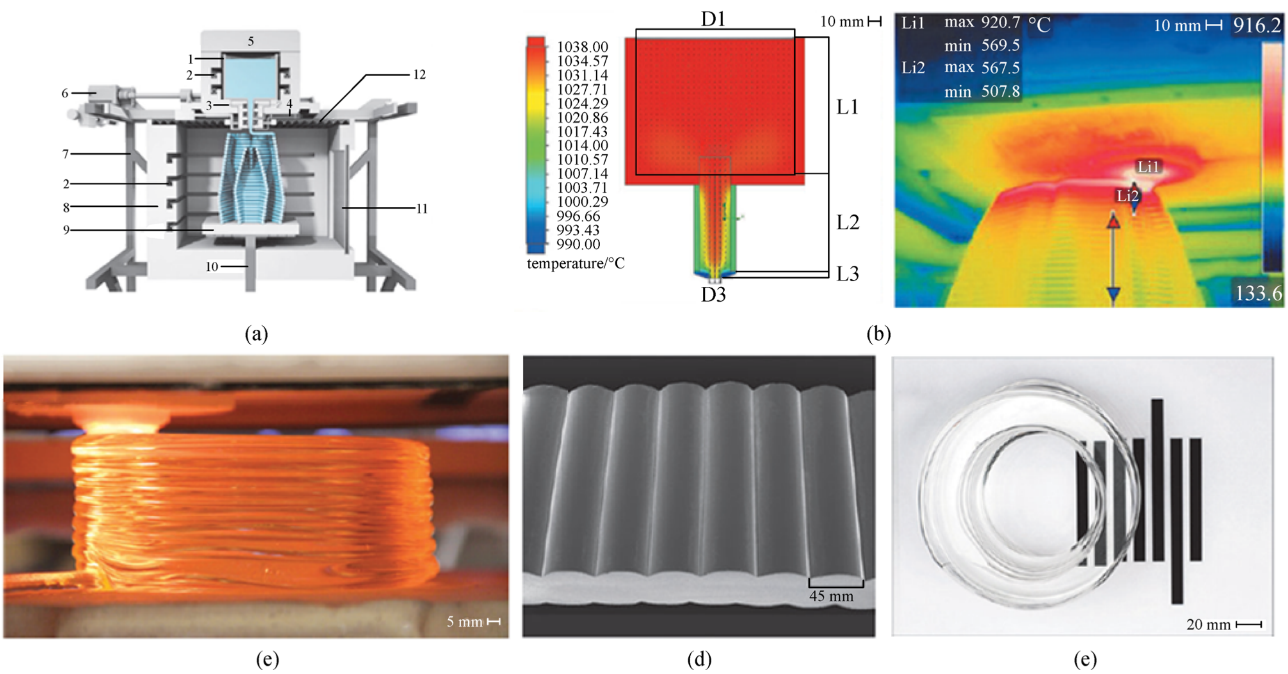


Fig. 1 (a) Cross section view of the structure of the 3D printing system that is based on the FDM technique. (b) Temperature distribution around the nozzle during the printing process. (c) Photograph of the nozzle during printing. (d) SEM image of a 3D printed glass sample. (e) Optical transparency of printed glass parts (top view of a 70 mm tall cylinder). Reproduced from Ref. [30]

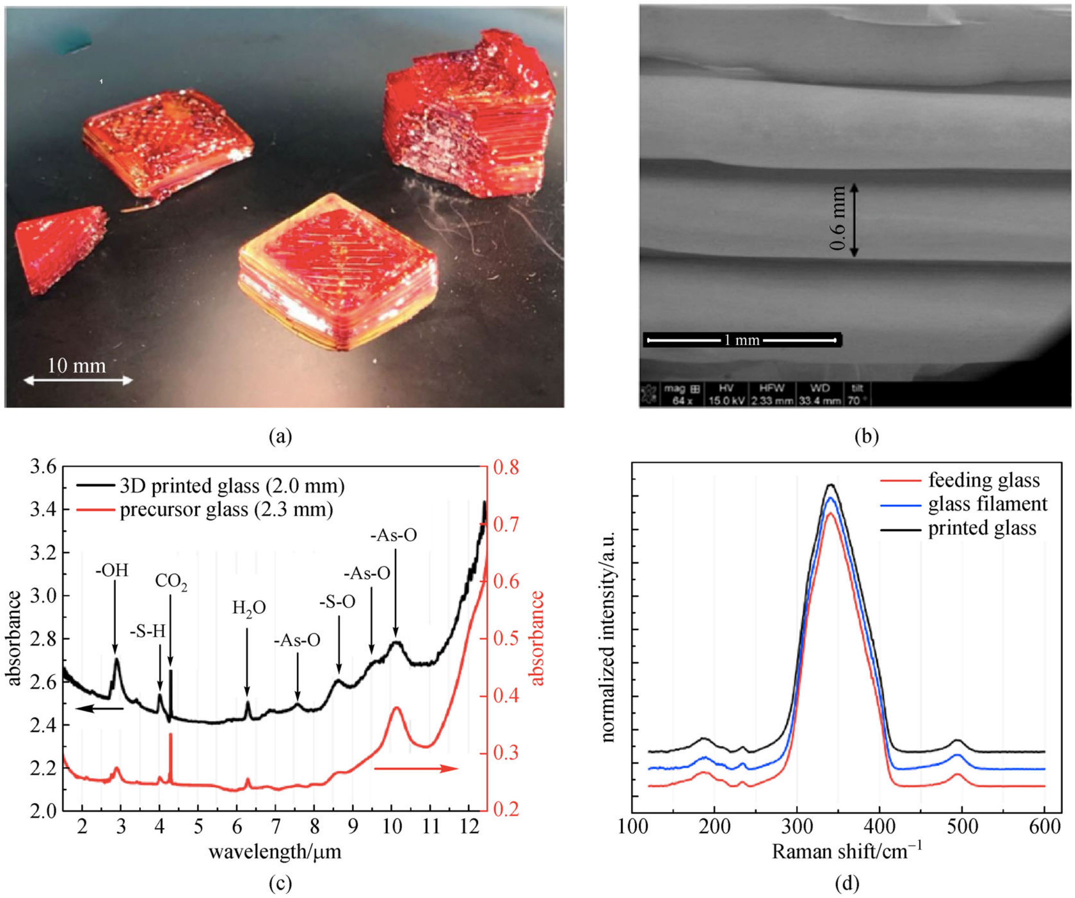


Fig. 2 (a) Photograph of 3D printed chalcogenide glass samples with the composition of $As_{40}S_{60}$. (b) SEM image of the printed $As_{40}S_{60}$ chalcogenide glass. (c) Absorption spectra of an unpolished $As_{40}S_{60}$ printed chalcogenide glass sample (with the thickness of approximately 2 mm) and of a polished slice of the $As_{40}S_{60}$ precursor glass (2.3-mm thickness). (d) Raman spectra of the original $As_{40}S_{60}$ chalcogenide glass, glass filament, and printed samples. Reproduced from Ref. [31]

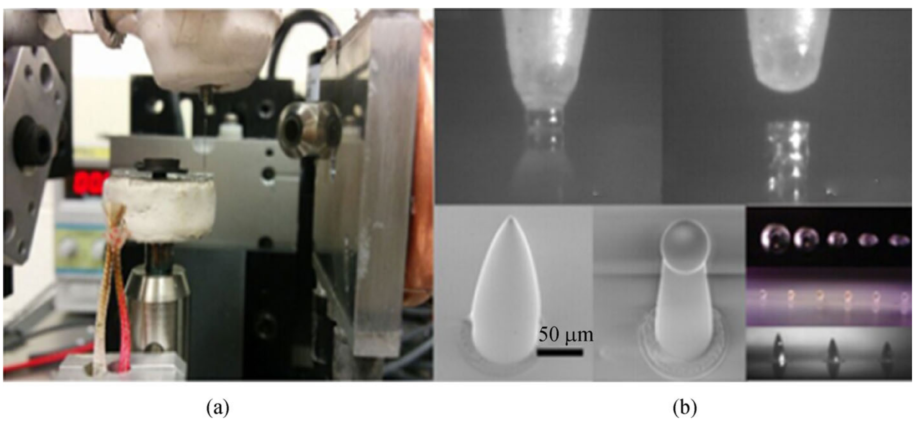


Fig. 3 (a) Photograph of a 3D glass printing system. (b) SEM images of 3D printed glass. Reproduced from Ref. [32]

The FDM technique is used to manufacture glass devices with complex shape, high transmittance, and favorable optical and mechanical properties. However, currently, 3D printing of glass by the FDM technique is still challenging. The operating temperature considerably affects the printing process of FDM, which makes it difficult to accurately control the discharge form and printing effect. Typically, printed samples have low precision, and the edge of each layer is prone to the "step effect" caused by layered deposition, which results in poor quality of the final products [25,33,34]. Owing to the limitations of the technique and material [35,36], the mechanical strength of printed objects is low; specifically, the tensile strength along the *Z* axis is relatively weak and does not meet industrial standards [37,38]. In addition, because glass printed by the FDM technique is printed step by step according to the shape of the cross section, the printing process is subjected to certain restrictions, and the production time is long; therefore, this technique is not suitable for the manufacturing of large objects. Compared with other 3D printing technologies, there are still many problems in using the FDM technique to print large-sized glass parts.

2.2 Stereolithography and digital light processing

Stereolithography (SLA) and digital light processing (DLP) techniques are both based on UV curing of photosensitive resins; however, these techniques differ in the process of printing 3D objects.

DLP is a rapid prototyping technique that uses a projector to solidify light-sensitive polymer liquids layer by layer to create 3D printed objects [39]. During the printing process, the 3D model is first sliced horizontally into layers by the 3D printing software; then, the shaped light pattern of the first layer of the 3D model is projected onto the liquidus photosensitive resin in one layer using the DLP projector to cure the photosensitive resin. After the first layer is printed, the printing platform and the printed object are both elevated at the same time; then, the projector projects the shape pattern of the next layer of the 3D model onto the photosensitive resin. The above-mentioned process is repeated, and finally the 3D glass object is obtained [40].

Instead of using a light projector, SLA is a rapid prototyping technique that uses an ultraviolet laser to solidify photosensitive polymer liquids layer by layer to create 3D printed objects. SLA printing does not simultaneously cure the entire layer of a 3D model pattern; instead, the resin is solidified point-by-point by scanning the focused laser light to form a curing layer. The main components of SLA photocurable 3D printers are similar to those of DLP printers, including an elevatable printing platform. When the first layer of photosensitive resin is solidified, the platform will be elevated by a certain distance; then, the second layer will be printed with the laser; this process is repeated until the printing process is completed [41,42].

SLA and DLP techniques can be used to produce glass parts with a small size, high precision, excellent permeability, and superior mechanical properties [43–46]. Therefore, it is also considered to be the most promising technique for 3D glass precision printing. The key to printing glass devices using SLA/DLP techniques is the design and fabrication of the slurry, which must have proper rheological properties while containing high concentration of SiO_2 nanoparticles. Currently, there are only few resin pastes that meet the above-mentioned requirements; in addition, the only material available for printing is SiO_2, which limits the application of SLA/DLP techniques in 3D printing of glasses.

In 2017, Kotz et al. [42] have fabricated 3D glass objects by the SLA technique. First, they dispersed SiO_2 nanoparticles with an average diameter of 40 nm in a mixed solution containing hydroxyethyl methacrylate monomers to form a glass slurry and printed a green part with an SLA 3D printing device. Then, the green part is heat-treated to achieve debinding and densification to form a pore-free, fissure-free, and transparent glass sample at 1300°C (Fig. 4(a)). Moreover, they demonstrated the application of this technique for the fabrication of glass microfluidic devices and doping of 3D glass parts with metallic salts such as $Cr(NO_3)_3$, VCl_3, and $AuCl_3$ (Figs. 4(b), 4(c), and 4(d)).

To print objects with complex structures, it is often necessary to add support structures to the objects. Currently, the commonly used methods for removing the support structures are as follows. 1) Select a support structure that can be easily removed during the slicing process; 2) carefully remove the support structure from the printed objects using organic solvents or polishing equipment. However, the use of the support structure increases the cost and time of printing objects, and it is easy to damage the printed objects while handling the support structure. Therefore, the use of support structures should be minimized [42,47,48].

Liu et al. [43,48] have developed a slurry for 3D SLA by dispersing silica nanoparticles with an average particle size of 50 nm in the mixed solvent of hydroxyethyl methacrylate (photosensitive monomer), tetraethylene glycol diacrylate (crosslinking agent), and benzoin dimethyl ether (photo-initiator). As shown in Fig. 5(a), the glass slurry was used as the raw material, and the bulk culture was printed with the rapid prototyping machine under the laser power of 70 mW and the scanning rate of 2000 mm/s. The green parts were immersed in isopropyl alcohol for 1 min to remove the surface attachment. Then the green part was heat-treated to remove organic matter and sintered to form a pore-free, fissure-free, transparent glass sample at 1250°C. The transmittance of the glass sample is up to 80% in the visible light range, which confirms its good optical performance (Fig. 5(b)). In addition, Liu et al. have successfully doped rare earth ions (e.g., Eu^{3+}, Tb^{3+}, and Ce^{3+}) into glass by soaking it in solutions containing these ions; the obtained 3D glass objects can emit red, blue, and blue light, respectively, under the excitation of a 254 nm UV lamp. This result implies the possibility of designing both the shape and function of a single glass device by 3D printing (Fig. 5(c)).

The printing speed of SLA differs from that of DLP. Typically, SLA has a very slow speed owing to the spot-on aggregation approach [49,50]. An increase in the printing speed of the SLA method using a higher laser scanning rate may affect the overall strength of the products and may

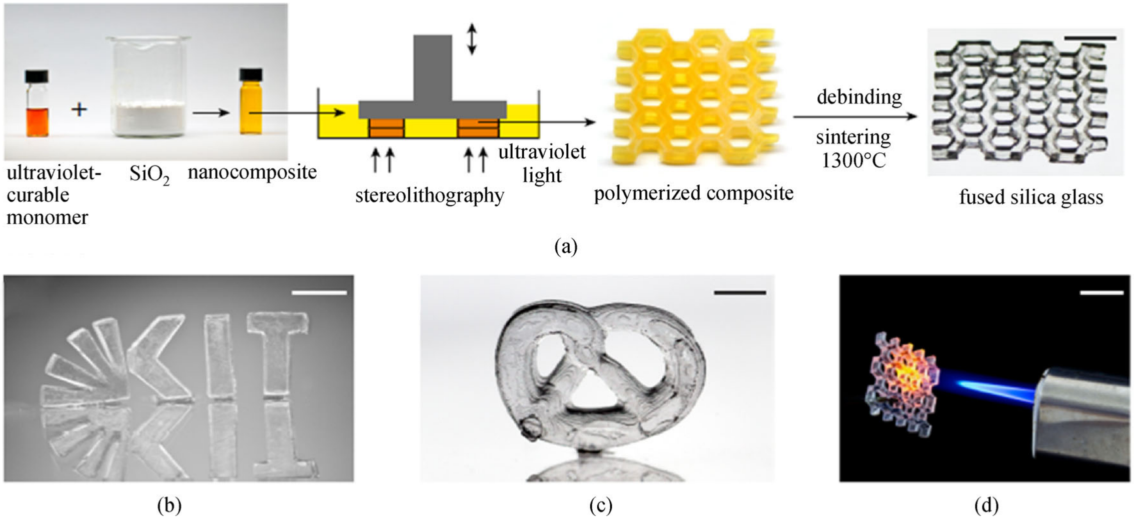


Fig. 4 3D printing of fused silica glass. (a) Ultraviolet-curable monomer mixed with amorphous silica nanoparticles is structured in a stereolithography system. The resulting polymerized composites transformed into fused silica glass through thermal debinding and sintering (scale bar, 7 mm). (b) and (c) Examples of printed and sintered glass structures: Karlsruhe Institute of Technology (KIT) logo ((b) scale bar, 5 mm) and pretzel ((c) scale bar, 5 mm). (d) Demonstration of the high thermal resistance of printed fused silica glass (scale bar, 1 cm). The flame had the temperature of approximately 800°C. Reproduced from Ref. [42]

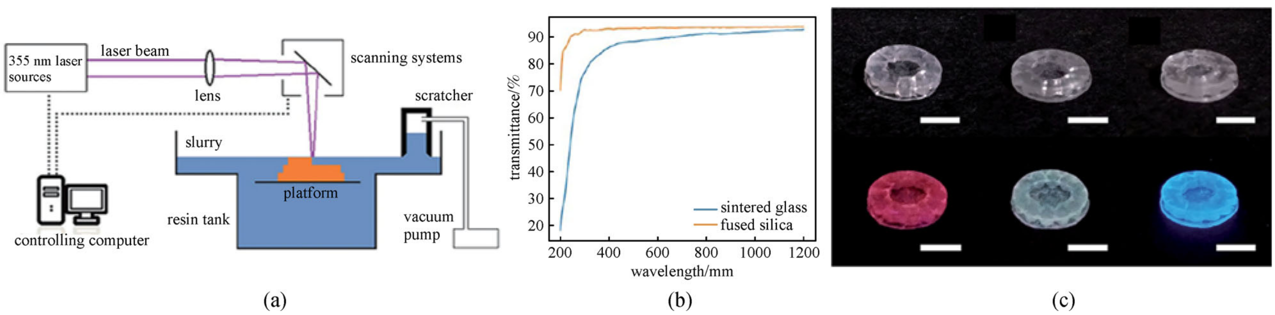


Fig. 5 (a) Schematic illustration of the stereolithography system for glass AM. (b) Transmittance spectra of sintered silica glass and fused silica. (c) Photographs of the additive manufactured silica glass doped with Eu^{3+}, Tb^{3+}, and Ce^{3+} and their photoluminescence under irradiation with a 254 nm UV lamp (The scale bars represent 5 mm). Reproduced from Refs. [43,48]

complicate post-curing processing. In comparison, the DLP technique allows the simultaneous solidification of the entire surface of the layer, without any difference between the edge and internal area, and post-solidification is not required. Typically, for the same 3D model file, DLP requires 60 min, while SLA requires 9 h to finish the printing process.

Moore et al. [51] have developed a new method for 3D printing of multifunctional glass using a DLP printer. In their method, UV light is used to control the phase separation and polymerization of liquid, which allows to control the porosity of the resultant multicomponent glass. In this method, Moore et al. added a second phase of a miscible liquid or polymer precursor to induce phase separation during polymerization (Figs. 6(a) and 6(b)). By adjusting the miscibility of the liquid, a polymer with a self-generated nanostructure can be obtained (Fig. 6(c)). Subsequently, the second phase can be removed by evaporation or thermal decomposition, which results in the formation of a porous structure of the polymer (Fig. 6(d)). The resulting nanostructured product is determined by the phase separation process, which depends on the mixing ratio and polymerization conditions of the precursor.

In their experiment, the researchers used the above-mentioned method to generate a porosity gradient in a variety of multicomponent glasses. The glass is made from a semi-organic alcohol precursor, which can be mixed with phosphorus and boron sources to produce multicomponent silicate, phosphate, and borate glasses. The phase transition liquid is acrylate, which is removed by pyrolysis before sintering the glass. These components are mixed into a single precursor solution, and the glass components are produced using a classical stereolithographic process.

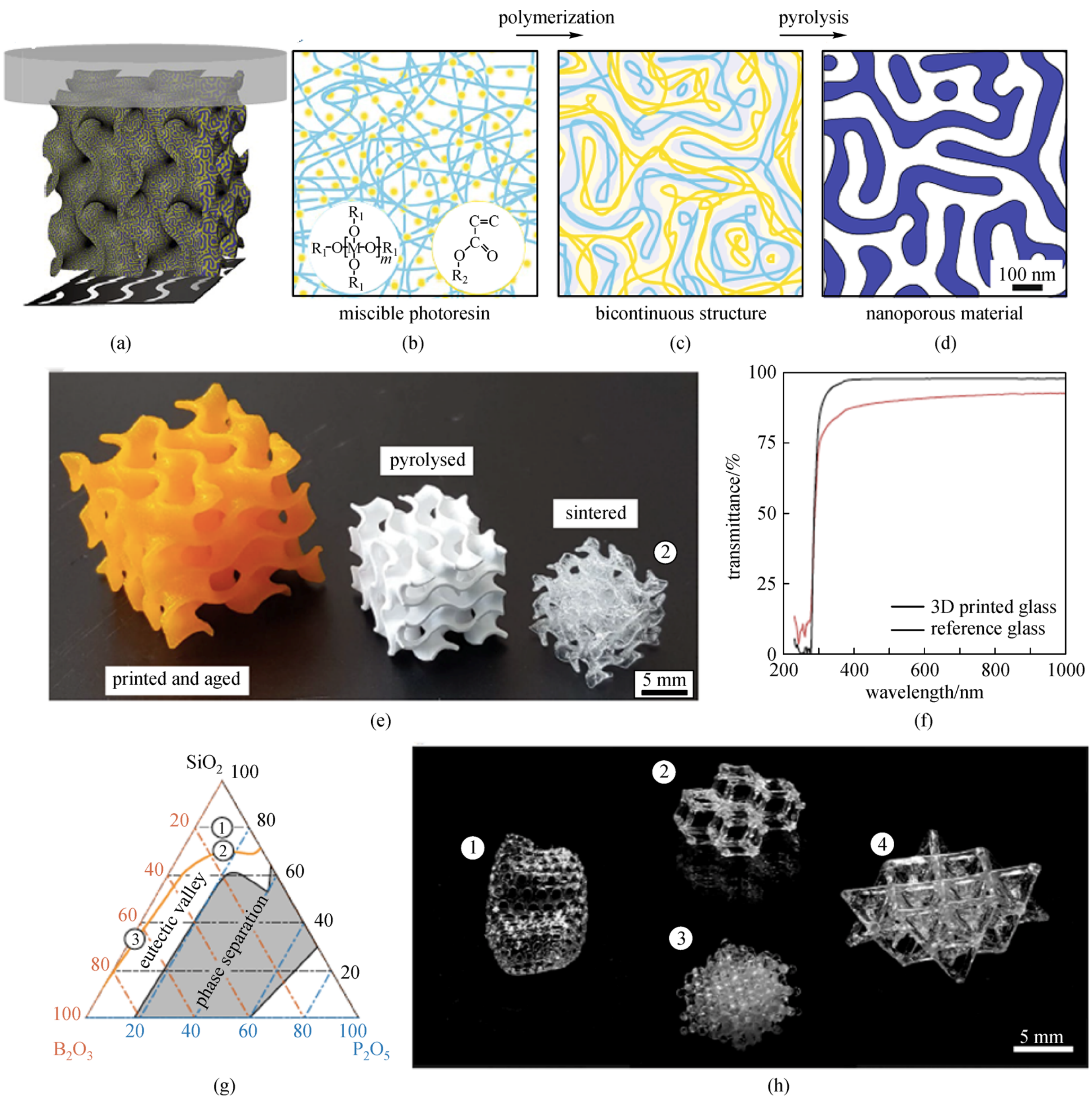


Fig. 6 (a) Schematic diagram of the process, which illustrates the geometrical complexity generated by the illumination pattern and the nanostructure emerging from the phase separation phenomenon. (b) and (c) During this process, acrylate monomers and pre-ceramic precursors, such as poly(diethoxysiloxane), are photopolymerized to form a three-dimensionally defined bicontinuous structure of organic and preceramic polymers. (d) The as-printed object is pyrolysed to form a nanoporous structure that can be optionally further sintered into transparent multi-material glasses and glass-ceramics. (e) Illustrative picture of a complex-shaped object at different stages of the process. (f) Optical transmittance of the 3D printed glass in comparison to a highly transparent reference. (g) Phase diagram of the boro-phospho-silicate system indicating the glass composition used to print the objects shown in this figure. (h) Transparent and dense boro-phospho-silicate glasses obtained by sintering 3D printed porous objects. Reproduced from Ref. [51]

In addition, this technique can print complex glass shapes with functional components of polyoxides. The pyrolytic nanoporous object was sintered at a higher temperature to form the morphology of complete dense phase separation (Fig. 6(e)). These glasses exhibit high transparency (Fig. 6(f)). An appropriate concentration of the inorganic precursor was selected to prevent crystallization, which resulted in glass formation under a moderate cooling rate (Fig. 6(g)). Combined with the above-mentioned control means, 3D glass objects with high transparency can be printed in a variety of complex geometric and multicomponent structures (Fig. 6(h)). This technique has been used in a wide range of applications, such as for the fabrication of catalyst carriers, monomers in chromatography, and filters and membranes used at high temperature and in harsh environments.

Cooperstein et al. [52] have developed a sol ink used for the 3D printing of transparent silica objects. In their printing process, the object is first printed by a commercial DLP printer (Fig. 7(a)). Then, the printed object (Fig. 7(b)) is dried at 50°C for five days (Figs. 7(c) and 7(e)). Finally, after a sintering process at 800°C for 60 min, a transparent silica structure is obtained (Figs. 7(d) and 7(f)). The SEM picture in Fig. 7(g) shows smooth surfaces of the silica structure.

Compared with the SLA technique, the DLP technique has considerable advantages in speed and accuracy [41,52]. Despite the clear advantages of the DLP method, currently, it is not possible to outperform the SLA method owing to the maximum printing size. The DLP process employs pixelated projection; thus, the print size is limited by the projector or liquid crystal display screen. In comparison, SLA 3D printers are different, and the size of produced objects can be as large as those produced by FDM 3D printing.

2.3 Selective laser sintering/melting

In recent years, with the rapid development of laser processing techniques, the research on 3D printing of glass by laser is gradually increasing [53–55]. SLM is a 3D printing technique that uses high power lasers to selectively melt powder materials. Using a similar principle of SLM method for metals, 3D printing of glass can be realized by SLM using glass powders. In this process, a layer of glass powder tile is formed by spreading powder on the surface of substrate or molded parts. Then, a high-energy laser beam is controlled to scan and melt a glass powder layer according to the corresponding layer section contour. After a cross section layer is melted, the workbench moves downwards, and another layer of glass powders is melted and printed. This process is repeated until the printing process is finished. Finally, the as-printed parts are heat-treated at designated temperature, time, and pressure [56–58].

Klocke et al. [59] have used the SLS process to directly process a borosilicate glass powder with an average particle size of 30 μm and a wide particle size distribution; they studied the influence of laser power, layer thickness, scanning speed, and other process parameters on the density and surface roughness of printed samples. The results showed that cracks in the sample appeared when the laser power was too high. When the layer thickness was too large, the surface roughness of the sample was higher. The sample density decreased with an increase in the scanning speed. The printed sample experienced a clear shrinkage after the heat treatment at temperatures between 600°C and 800°C.

Compared with ceramic and metal materials [49,59–62], glass materials are more difficult to process by 3D printing. This occurs because glass materials have high melting points and low thermal expansion coefficients, which leads to the formation of cracks and pores during the printing process. To overcome these problems, it is required to accurately control the temperature of the glass melt, which makes it challenging to realize high-precision 3D printing of glass.

Luo et al. [63–65] have used the SLM technique for 3D

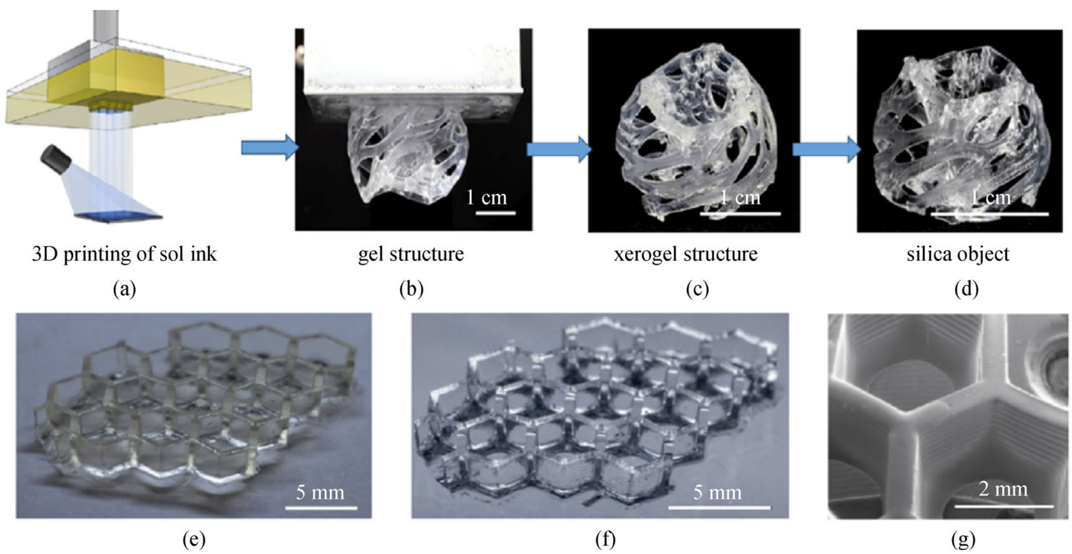


Fig. 7 Schematic diagram of 3D printing that is based on a sol ink and the obtained transparent silica glass objects. (a) Printing of the sol gel ink by a DLP printer. (b)–(d) Printed structures composed of 15 wt% of S1 and 13.3 wt% of 3-acryloxypropyl trimethoxysilane (APTMS) at different stages: (b) wet gel structure after printing; (c) dry structure after the removal of solvents (drying at 50°C); (d) silica structure after burning away organic residues at 800°C. (e) Structures printed with ink composed of 15 wt% of S1 and 5.3 wt% of APTMS. (f) Transparent silica object after burning away organic residues at 800°C. (g) Environmental scanning electron microscopy (ESEM) image of the 3D printed silica object. Reproduced from Ref. [52]

printing of soda-lime silicate glass. First, they used a laser to fuse a mixture of the glass powder to study the melting and aggregation of powder at different laser energies. Then, the laser was used to perform a 3D line scan for 3D printing, and the processing parameters were optimized for the fabrication of a transparent glass object by printing (as shown in Figs. 8(a) and 8(b)). The transparency of the fabricated product is comparable with that achieved by traditional methods. Luo et al. examined the impact of key process parameters on the morphology and optical properties of the printed glass and established a thermal field model for the melting region to explain their experimental results. On the basis of the abovementioned experiments, they designed and printed several optical devices (e.g., a single wall, a cylinder, and a cube), as shown in Figs. 8(c), 8(d), and 8(e). However, in these optical devices, the surface quality of molded parts is poor, and the products need to be processed again. In addition, spheroidization and warping have also appeared in these objects, which need to be solved.

The SLM technique for 3D printing of glass provides a new method for the fabrication of glass objects with arbitrary shapes, which is promising for many potential applications. The technique can be used for the fabrication of glass artworks; however its precision needs to be improved to produce precise optical devices.

2.4 Direct ink writing

Direct ink writing (DIW) is an emerging 3D printing technique. This technique works by extruding a semi-solid ink material with shear thinning properties from the print nozzle. Then, the ink is rapidly solidified by gelation, evaporation, or temperature-induced phase change. Next, the green body is subjected to a series of heat treatment and sintering processes to produce the required glass components [66,67]. The essential step of printing glass devices by the DIW technique is the synthesis of ink with dispersed glass powders. For the synthesis of ink, the following requirements have to be fulfilled. 1) The ink must have good rheological and shaping properties; 2) ink gelation should not result in pore formation during the drying process and can be completely densified and removed [67]. Compared with the FDM technique, the DIW technique does not require high temperature to print glass [30,31].

Nguyen et al. [68] have mixed silica nanoparticles with tetraglyme and hydroxyl-terminated dimethylsiloxane to form an organic paste and printed a preset green part by the DIW technique; then, the part was heat-treated and fired into glass components. The results show that this method allows to print glass devices with different microstructures. Using silica sol as the raw material, Destino et al. [69] have prepared silica glass with high transmittance (> 90%) and good optical performance by the DIW method. The schematic diagram of the method and the transmittance spectra are shown in Fig. 9. Dudukovic et al. [70] have developed an ink system with adjustable rheological properties, and they demonstrated 3D printing of a multicomponent SiO_2–TiO_2 glass with a varying spatial refractive index.

Recently, Sasan et al. [71] have demonstrated germania–silica glasses with excellent optical quality that were fabricated by 3D printing. They described a method for the production of colloidal germanium dioxide raw material

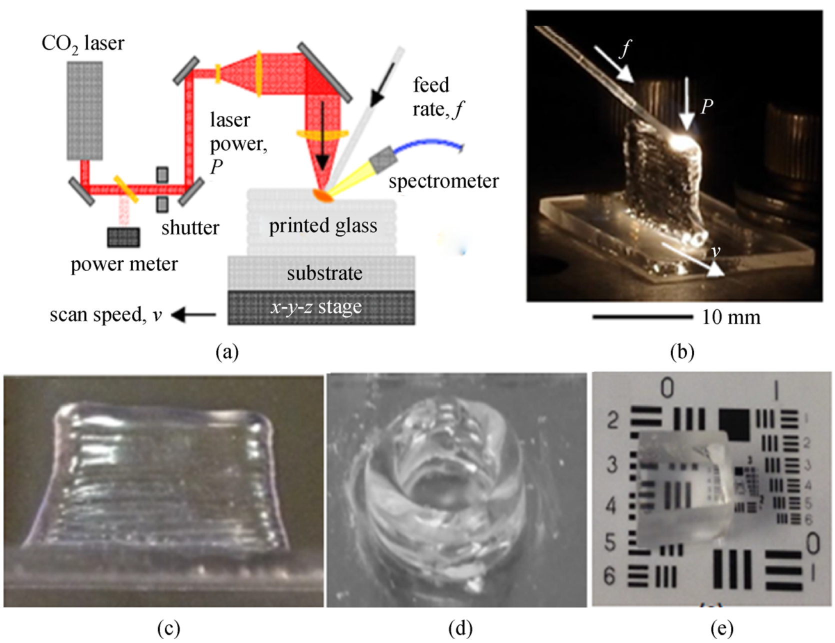


Fig. 8 (a) and (b) Illustration and photograph of the filament-fed fused quartz AM process. (c) Single wall printing. (d) Photographs of the printed fused quartz cylinder. (e) Photographs of the printed cubes. Reproduced from Refs. [63–65]

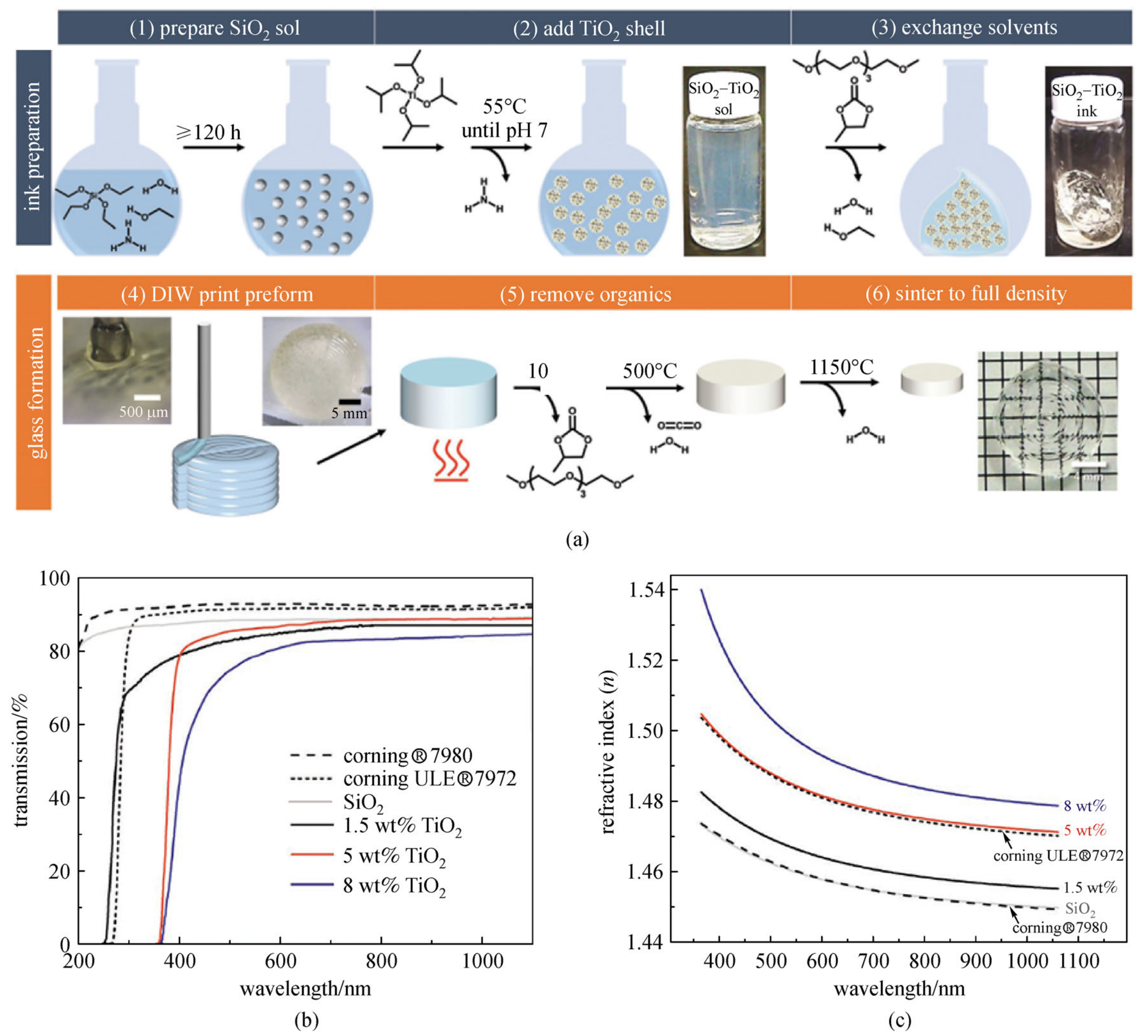


Fig. 9 (a) Schematic diagram for the sol–gel-derived DIW SiO_2/SiO_2–TiO_2 glass fabrication. (1) SiO_2 particle sol preparation. (2) TiO_2–SiO_2 core–shell particle preparation. (3) Ink preparation by solvent exchange from the particle sol to DIW printable ink. (4) DIW printing of a glass preform. (5) Organic removal to low density inorganic glass preform. (6) Sintering to full density optical quality glass (unpolished). (b) UV–vis optical transmission spectra. (c) Optical dispersion curves. Reproduced from Ref. [69]

particles that were suitable for mixing with various silica colloids to change the refractive index. Then, they described the process by which the colloidal particles are converted to inks, printed by DIW, and then converted to glasses with varying germania concentrations. Finally, they characterized the printed GeO_2–SiO_2 glasses to show how they compared to those prepared by conventional methods in terms of chemical composition, optical transmission, and refractive index.

The DIW system operates under relatively moderate temperatures to print glass parts with good transparency, zero porosity, and sub-millimeter size. Moreover, the advantages of the DIW method is that it can be carried out at room temperature without heating, laser, and ultraviolet radiation. However, the accuracy of the sample is usually limited by the diameter of the nozzle, and the deposited pattern is limited by the path of the nozzle. In addition, printed embryos usually require a long time to dry; these limitations considerably hinder the application of the direct ink writing 3D printing technique [71,72].

3 Applications and challenges

3.1 Applications

With the rapid development of the 3D printing technique, various 3D printing glass technologies have been developed. Compared with traditional glass manufacturing methods, the 3D printing glass technique has two major advantages. First, the 3D printing glass technique can produce glass devices with complex shapes and structures, which are not accessible by traditional glass. Second, the 3D printed glass technique allows glass to be processed with high precision at the sub-millimeter level. These two advantages allow the 3D printing glass technique to be widely used to make sophisticated glass ornaments [17], optical components [18,66], and microfluidic chips [18]. Herein, we discuss the recent application of 3D printing glass.

3.1.1 Glass ornaments

Owing to the high transparency, glass materials are widely used to make ornaments of various shapes and sizes. Conventionally, it is difficult to fabricate hollow structures by traditional die pressing, but it is easy to fabricate these structures by 3D printing. Figure 10 shows the typical glass objects prepared by the 3D printing technique [17,42]. These results show the wide application of 3D printed glass for personalized crafts.

3.1.2 Optical elements

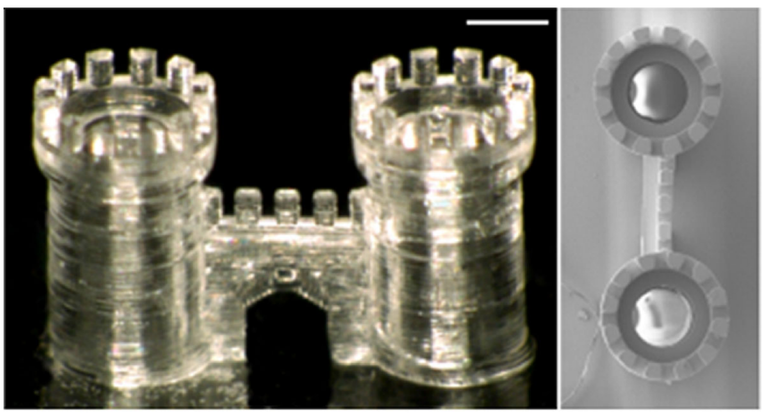
Traditional micro-optics devices are usually manufactured by die-pressing. In this process, an exact mold is first prepared; then, the molten glass is filled into the mold for hot pressing to form a glass device with a preset geometric structure. The entire process is time-consuming and tedious, and it is also difficult to process glass devices in the sub-millimeter size [17,18].

However, 3D printing can overcome these limitations. 3D printing of optic components does not require expensive molds, fixtures, and post-processing [73–75]. Because there are no traditional design and manufacturing process constraints, this unique process greatly improves the speed and flexibility of optical devices in production. In addition, 3D printing allows optical devices to be made with variation in geometry and composition, which cannot be achieved using traditional manufacturing methods. For example, 3D printing techniques can be used to create lenses with an index gradient that can be polished, which will replace the more expensive polishing technique used for traditional curved lenses [76–78].

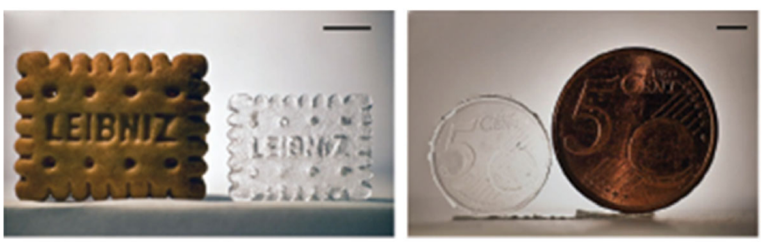
Currently, there are typically two strategies to make optical components using 3D glass printing techniques. The first approach is to directly manufacture two-dimensional or three-dimensional optical component structures, which show specific diffraction, scattering, and other functions [42]. Typical optical components printed by 3D printing techniques are shown in Figs. 11(a) and 11(b). The second approach combines other materials to produce optical components with a gradient distribution of refractive index [68] (as shown in Fig. 11(c)).

3.1.3 Microfluidics

Microfluidics is based on the precise control of microscale fluid, which is also known as a laboratory-on-a-chip or a microfluidic chip technique; microfluidics integrates basic operation units (e.g., sample preparation, reaction, separation, and detection of biological, chemical, and medical



(a)



(b)

Fig. 10 (a) Microstereolithography of a hollow castle gate (scale bar, 270 μm). (b) A cookie (scale bar, 7 mm) and a coin (scale bar, 4 mm) were successfully replicated and printed in glass. Reproduced from Refs. [17,42]

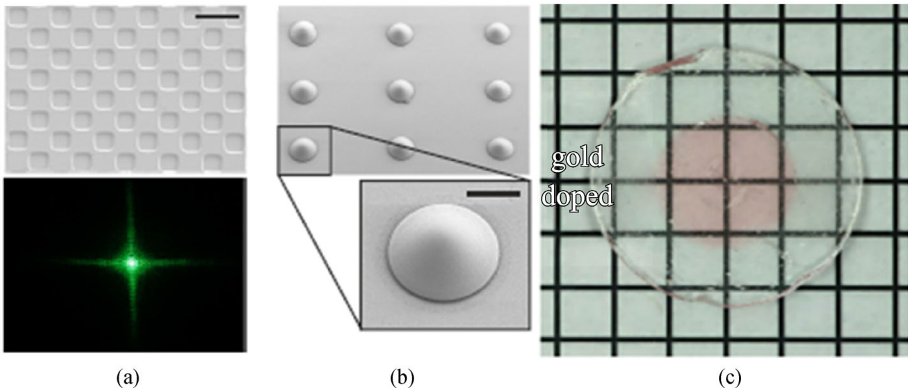


Fig. 11 (a) Micro-optical diffractive structure, which creates the optical projection pattern shown at the bottom (illuminated with a green laser pointer; scale bar, 100 μm). (b) Micro lenses fabricated using greyscale lithography (inset scale bar, 100 μm). (c) 3D printed multicomponent glass. Reproduced from Refs. [42,68]

analysis processes) into a micrometer chip and automatically completes the entire analysis process [79,80]. Owing to its potential applications in diverse fields, it has been actively involved in the fundamental research in biology, chemistry, medicine, fluid, electronics, materials, and machinery [17,78,81–83].

Currently, the mainstream microfluidic material is polydimethylsiloxane (PDMS). However, PDMS is a thermoelastic polymer material, which is not suitable for industrial injection molding and packaging process. Moreover, PDMS microfluidic batch manufacturing is costly. In comparison, glass has good physical and chemical stability which is an ideal substitute for PDMS [79,84–87]. 3D printing technique enables rapid manufacturing of micro-fluid channels in a few hours, which is highly attractive for microfluidic-based research. Figure 12 shows several microfluidic glass chips that have been recently created with the 3D printing technique [17,18].

3.2 Challenges

As one of the most important materials in the 21st century, glass is ubiquitous in our daily life, from the smartphones to fiber optic components that provide Internet access to billions of households. Life without glass is unimaginable. However, despite the many advantages of 3D printing

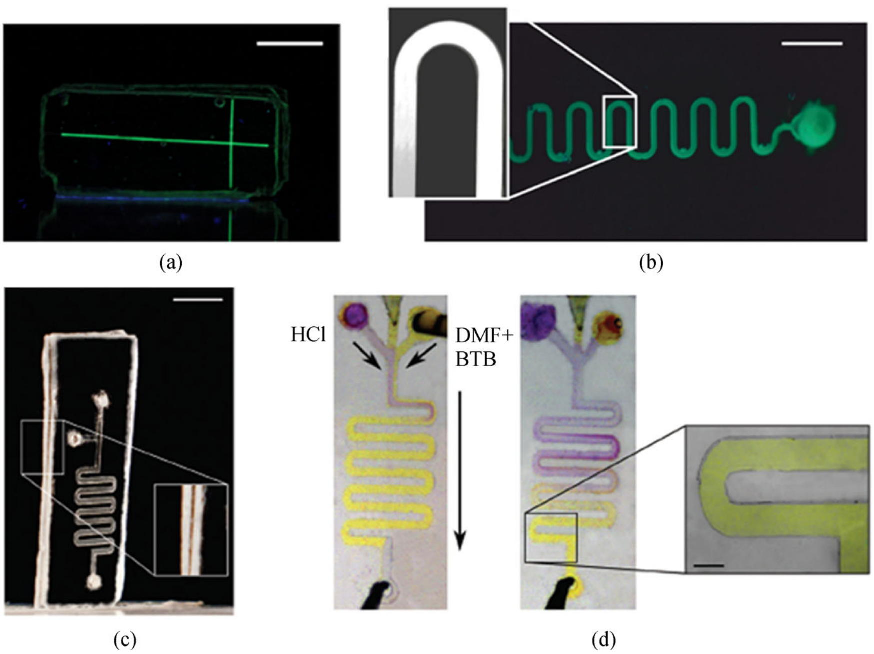


Fig. 12 (a) Microfluidic fused silica chip fabricated by 3D printing; a nylon thread is embedded into the channel (scale bar, 9 mm). (b) Microfluidic zigzag (scale bar, 11 mm). (c) Two-layer microfluidic glass chip (scale bar, 4 mm). (d) Microfluidic chip with its channel filled with colored solutions (scale bar, 350 μm). Reproduced from Refs. [17,18]

techniques, the available materials for 3D printing are still limited. Currently, 3D printing is mainly applicable to plastic products and a small number of metal products, while glass materials are basically not suitable for 3D printing.

The difficulty of 3D printing of glass objects can be attributed to the inherent nature of glass, especially its high brittleness. In addition, the loss of transparency owing to the presence of pores formed during printing and sintering remains a tremendous challenge for the practical application of 3D printed glass objects.

In addition, there are many problems to be solved in various 3D printing glass technologies. In the FDM technique, glass usually needs to be heated to more than 1100°C, and an accurate temperature control of the heating apparatus is required during the printing process to ensure the successful printing of objects. In addition, owing to the disadvantages of the FDM technique, the printed objects still have the problems of low accuracy and low strength. For SLS/SLM techniques, the material for 3D printing is a glass powder, which results in poor surface quality of printed objects. Moreover, the high cost of high-power lasers and precision optical instruments also limits the use of this technique. The glass objects printed by SLA/DLP techniques have the advantages of high precision, high stability, and high optical transmittance; these techniques are considered to be the most promising technologies for 3D printing of glass. However, currently, few materials are available (only SiO_2) for printing using this technique, which severely limits its use. For the DIW technique, the accuracy is usually limited by the diameter of the nozzle, while the deposited pattern is limited by the movement path of the nozzle. In addition, the printed embryo body requires a considerable amount of time to dry. These problems severely hinder the innovation and application of the DIW technique.

4 Summary

With the development of 3D printing techniques, there is growing interest in their application for the fabrication of glass objects. The 3D printing of glass technique broadens the range of materials available for 3D printing. Moreover, it provides facile strategies for the high-precision fabrication of otherwise complex structures made of glass. Therefore, 3D printing techniques have brought new life to the ancient material, glass. 3D printed glass objects can be used as optical components and microfluidic chips, which is beyond the conventional use of glass. However, there are still many challenges associated with 3D printing of glass such as the relatively limited printable glass systems, complex and time-consuming printing process, limited precision, and high cost. In addition, the optical and mechanical properties of the printed glass still need to be improved for practical applications. The 3D printing of glass techniques are still in their infancy, and rapid future developments are anticipated to overcome these limitations in both printing methods and quality of printed objected. Nevertheless, we believe that the development of 3D printing techniques for glass will considerably affect the manufacturing of glass objects in the near future.

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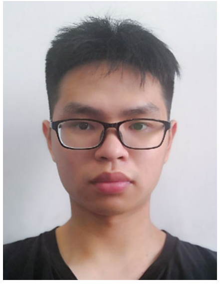

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