Journal of Computational Applied Mechanics 2025, 56(1): 69-75

DOI: 10.22059/jcamech.2024.380479.1185

RESEARCH PAPER

Advances, Limitations, and Future Perspectives in 3D Printing of Porous Glasses: A Technical Note

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Abstract

In this study, the latest developments in 3D printing of porous glasses are discussed. Current challenges in 3D printing of porous-based microfluidic devices mostly include the printing resolution which is correlated with the processing time, post treating, and developing tailored materials for porous glasses. Although the latter issue has been resolved to some extent recently, the former has remained a challenge. Currently, the smallest 3D printed feature in a microfluidic structure is 200μm while higher resolutions are required in some applications. On the other hand, previous reports have shown intensive printing time for higher resolutions. To achieve an optimal compromise, further investigations and technological advancements in the printing technology should be carried out. An extrusion-based 3D printing system "G3DP2" developed by MIT researchers enables the printing of porous glasses by controlling the heating and cooling cycles. The other important challenge is related to the printable glass materials. Recently, newly developed materials such as ceramic-based resins and "Glassomer" that contains fine glass powders in a plastic binder matrix, has enabled the fabrication of porous glasses by resin 3D printing systems.

Keywords: 3D printing, porous materials, microfluidic devices, glass materials;

1. Introduction

Due to large surface area and connected inner channels, porous substrates have found extensive applications in analytical instruments and biomedical devices. Hierarchically porous glasses (PGs) are currently being used for tissue engineering and drug delivery purposes. In general, hierarchically porous materials are broadly defined as those containing organized structural pores on multiple length scales [1]. PGs are also used in analytical instruments such as columns, filters and reactors, where intimate contact between solid and fluid phases is needed [2]. Although porous structures and particularly PGs can be utilized in microfluidic devices [3-5] but due to their small dimensions and complex shapes, their fabrication has remained a challenge. Besides, creating a desired pattern of pores (in terms of size, shape, and orientation) at micron scales is another challenge of fabricating porous-based microfluidic devices. As the form of a porous structure defines its function, it would be very beneficial if they could be fabricated accurately and in the desired form. For example, according to a study by *Schure and Maier* [6-8], face-centered cubic

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packing of spherical particles, leads to a lower reduced plate heights of chromatographic beds, compared to other arrangements [8]. In this regard, developing a suitable fabrication method could make a leap forward in the technology of microfluidic devices. Evard et al. [9] successfully examined the following printing methods to fabricate porous-based microfluidic structures: a) curing a porous monolithic polymer sheet into using photolithography, (b) screen printing silica gel particles with gypsum, and (c) dispensing silica gel particles with polyvinyl acetate binder using a modified 3D printer. However, some technical challenges related to printing technology, printing time, resolution, post processing, and printable glass materials have not been comprehensively investigated in the literature. This article takes a technical look at the advances and the challenges of using 3D printing of porous glass structures in microfluidic devices.

2. Fabrication methods of porous glass structures

Common methods for fabricating porous glass structures are dry pressing-sintering, phase separation, sol-gel process, foaming, polymer sponge replication, freeze casting, and 3D printing. Obtaining a uniform distribution in pore size, low dimensional accuracy of geometrical features, avoidance of crack formation due to the thermal expansions during thermal treatments, and high fabrication costs have limited the application of traditional techniques. Liao & Cheng [10] explored the potential of femtosecond laser micromachining to fabricate complex micro- and nanofluidic structures within porous glass substrates. They reported that while this technique allows for precise spatial control, the surface roughness of the microfluidic structures needs improvement to meet the standards required for in vivo and optofluidic applications. Additionally, they observed that the cross sections of nanochannels were highly elliptical and asymmetrical, indicating limitations in axial resolution and overall fabrication precision. Furthermore, they noted that the fabrication efficiency remains low for large-volume, high-aspect-ratio microfluidic devices, presenting a significant area for future development.

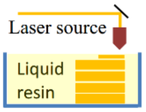
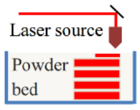
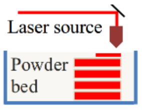
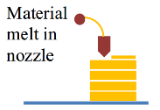
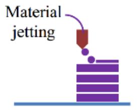
Compared to traditional methods, 3D printing technology offers better quality, robustness, and resolution. High resolution of some 3D printers alongside the controllability of the power source has enabled the fabrication of structures with a broader range of desired shapes and sizes. 3D printing simply comprises of three steps: 1- Designing a CAD model, 2- converting the CAD model to a set of commands that are interpretable by 3D printers and 3- construction of the model, layer by layer, by joining or solidifying the materials (in forms of liquid molecules or particles) together. The porous structure is first modeled in a CAD program and is saved as .STL file. This STL file contains the meshes, vertices, and orientations of thousands or millions of constructing elements of the structure. More elements with closer vertices means that more details have been captured in the model and it will demand higher resolution of the printer. This is crucial in printing microfluidic devices with complex details and features in their geometries. For porous-based microfluidic devices, the resolution of the printer should be high enough so that every important detail or feature of the pores is reflected in the final structure. At the next step, the material should be solidified layer by layer. The application of different 3D printing systems at microfluidic devices has been widely studied by *He et al.* [11].

2.1. 3D printing of porous glass structures

Porous structures are widely used in biomedical and microfluidic devices [12], such as bone scaffolds [13-15] and cell culture systems [16], due to their high surface area, excellent permeability, low relative density, and high specific strength. 3D printing techniques that have been used for the fabrication of porous structures mainly include Stereolithography (SLA), Selective Laser Sintering (SLS), Selective Laser Melting (SLM), Fused Deposition Modeling (FDM) and Binder based 3D printing (3DP). However, selective laser melting hasn't been used as widely as the other methods [11]. Table 1, illustrates each method with its characteristics.

In SLS and SLM methods, the solidification mechanism is through sintering and melting respectively using a laser beam. In SLM, powder particles are melted and bonded together in each layer while in the SLS method, they are sintered [17]. The FDM approach involves heating soda lime glass to approximately 1,000°C. This technique yields coarse structures with rough surfaces. However, it should be noted that 3D printing parameters greatly affect the surface quality of the final product [18]. Alternative methods, such as inkjet printing and selective laser melting or sintering of glass powders, have so far only produced white, non-transparent glass components [19]. Although FDM is a simple 3D printing method, it is not a suitable fabrication technique for ceramics and glasses that have high melting temperatures. Besides, the resolution of FDM is relatively low which is not suitable for microfluidic devices. In contrast, the SLA method offers better resolution and good surface quality that is advantageous for microfluidic devices. It is also capable of producing porous structures with acceptable quality. In SLA, 3D object is fabricated layer by layer from bottom to top. In each layer, liquid resin is photopolymerized by ultra-violet (UV) laser beam. For porous ceramics, ceramic suspension (in aqueous or non-aqueous media) is replaced with liquid resin [20] and after the completion of the polymerization stage, the process is followed by polymer burn out (pyrolysis) and sintering the ceramic body at high temperature [21-23].

Table 1: 3D printing methods for the fabrication of porous structures (Reprinted with permission from [20])

Techniques		SLA	SLS	SLM	FDM	3DP
Technique schematic						
Operating principle		Photo polymerization	Powder sintering	Powder melting	Melt extrusion	Powder + binder deposition
Characterizations	Surface quality	*Average*	*Good*	*Poor*	*Average*	*Good*
	Post-finish	*Average*	*Good*	*Average*	*Average*	*Good*
	Accuracy	*Excellent*	*Good*	*Poor*	*Average*	*Average*
	Resistance to impact	*Average*	*Good*	*Good*	*Good*	*Low*
	Flexural strength	*Low*	*Excellent*	*Excellent*	*Excellent*	*Low*
	Prototype cost	*High*	*High*	*High*	*Low*	*Medium*
	Post cure	*Yes*	*Yes*	*No*	*No*	*No*

In 2017, Kotz et al. [19] utilized a SLA-based approach to create transparent fused silica glass from silica nanocomposite materials. In their approach, ultraviolet-curable monomer is mixed with silica nanopowder and structured via stereolithography. The resulting composite is then converted into fused silica glass through thermal debinding and sintering. This method enabled high-resolution printing with a smooth surface finish, demonstrating potential applications in optical and industrial settings. Fig 1 demonstrates the 3D printing process utilized in their research.

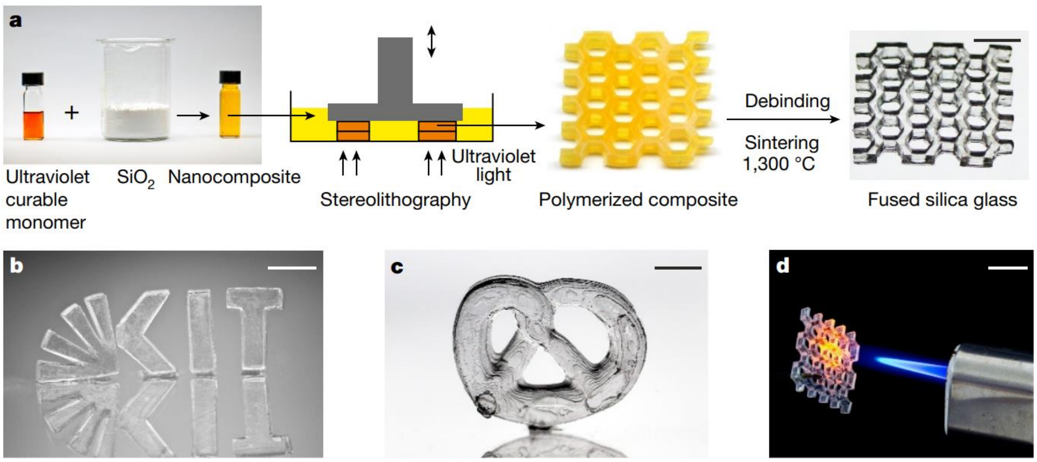


Fig 1: 3D printing of fused silica glass. Examples include a printed KIT logo and a pretzel structure (scale bar, 5 mm each). The high thermal resistance of the printed glass is demonstrated, withstanding an 800°C flame (scale bar, 1 cm) [Reprinted with permission from [19].

In 2018, MIT researchers have utilized a 3D printing technique for fabricating porous glass structures with intricated details [24]. They invented a system named G3DP2 for 3D printing of glass materials with complex geometrical shapes. This system that is an extrusion-based 3D printing system, is able to control the temperature during the various stages of glass formation. In three separate chambers, glass is first kept in fusion state at a temperature of 1090˚C to keep it fluid. But the second chamber and the printing chamber are maintained at 800 ˚C and 450˚C respectively. In fact, this process enables 3D printers to control the cooling and crystallization of glass. However, due to the high temperature of the process, it requires expensive heat-resistant equipment. In another attempt by Kotz et al. [25] a special nanocomposite ("Glassomer") consisting of a very high proportion of finest glass powder and a plastic binder was developed. Like other typical resins, this material can be used by the SLA printing method. After printing, the component enters the furnace (sintering stage) at temperatures lower the melting point of glass, the binder is removed and glass particles bond together. This process enables available SLA printers to fabricate glass-based microfluidic devices. In 2020, Moore et al. [26] developed a 3D printing platform based on photopolymerization-induced phase separation that can be implemented in commercially available DLP systems [26]. In their study, different pore sizes and structures are formed by adjusting the light intensity. Just like the previous method, after printing, the component is treated at 600 ˚C and 1000 ˚C respectively to burn off the polymer and to densify the ceramic structure into glass. The progress of a sample porous glass at different stages is shown in Fig 2.

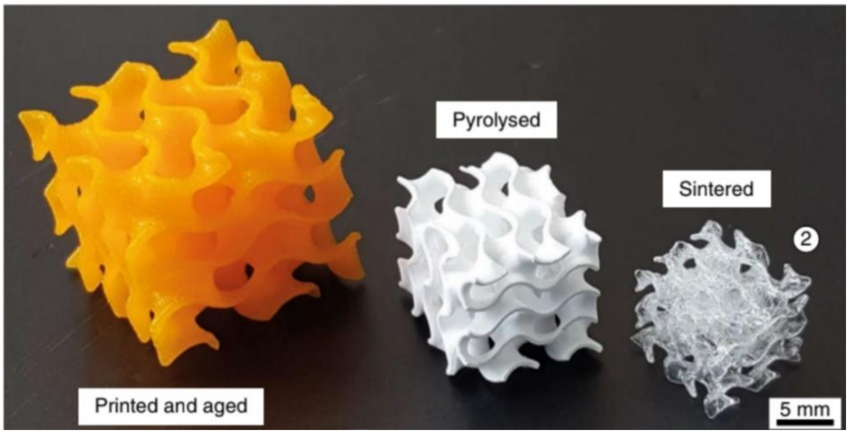


Fig 2: Porous structure before heat treating (left), after being heated at 600 ˚C (middle) and after being further heated at 1000˚C (right) (Reprinted with permission from [26])

In a recent study in 2024, Li et al. [27] studied a novel approach to fabricating high-precision fused silica glass structures through one-photon micro-stereolithography (OμSL), utilizing PEG-functionalized colloidal silica nanoparticles and a specialized photopolymerizable resin. Notably, this approach allowed for a minimum feature size of approximately 2 µm, with capabilities for complex geometries without needing additional support structures. The printed samples underwent a heating and sintering stage at 1050°C under vacuum to eliminate the polymer matrix. The final fused silica product exhibited excellent optical transparency (95% transmission with minimal defects), remarkable compressive strength (up to 40.85 MPa), and minimum feature sizes of approximately 900 nm. Fig 3 illustrates glass micro-architectures fabricated using the proposed 3D printing technique.

2.2. Limitations of 3D printing of porous-based microfluidic devices

The application of 3D printing technology in the fabrication of microfluidic devices has been well studied in the literature [11, 17]. However, this technology has some significant limitations as well. These limitations are mostly related to the accuracy of printing (resolution) [28] and materials. In the following, some foreseeable limitations for 3D printing of porous-based microfluidic devices are discussed separately:

2.2.1. Resolution and time

In microfluidic devices, geometrical details become very important. Currently, the smallest reported feature on microfluidic devices that has been acquired by 3D printers is approximately 200µm [29] while smaller sizes are needed in some cases. In tissue engineering applications, porous structures should involve interconnected pores with diameters between 50 to 1000µm [30]. On the other side, the time required for printing an object increases with its size and resolution and it may take several days or even weeks to fabricate an object. For microfluidic devices, creating high-resolution features in micron scales requires a large number of thin layers and this will increase the total printing time.

2.2.2. Post-processing

Highest resolution 3D printing techniques usually need supporting materials to fill the void spaces and removing all the supporting materials is usually impossible. Low resolution has also a negative effect on the surface quality of the final product. It may create contour like shapes on the surfaces of the pore channels and micro-polishing might be required. Furthermore, removing all the supporting materials (for methods such as SLA) from the voids is not possible.

2.2.3. Materials

There are a limited number of materials that can be used for 3D printing. 3D printing of materials such as glass and silicon that are hydrophilic is very challenging. In 1998, PDMS (also known as silicon rubber) was first introduced as a replacement of glass and silica in microfluidic devices [31]. PDMS as a transparent material, is inert, non-toxic and non-flammable; more importantly, it cures at lower temperatures [32]. Although, soft lithography which is a replica molding process has been the most commonly used fabrication technique for PDMS-based microfluidic devices, this process yields materials with weak mechanical strength and low resolution geometrical shapes. Besides, it is a multi-step, time-consuming and labor-intensive process that makes it unsuitable for the manufacturing of microfluidic devices. Furthermore, due to the low elastic modulus of PDMS, it is very difficult to 3D print this material.

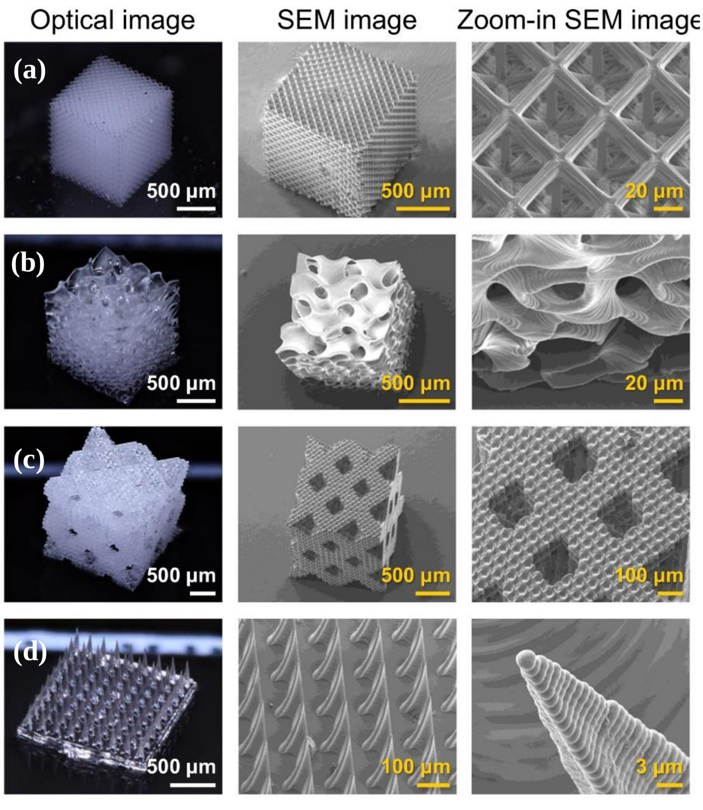


Fig 3: Transparent fused silica glass micro-architectures fabricated using the proposed OμSL technology. Optical and electron microscopy images depict several 3D-printed structures: (a) a 12 × 12 × 12 octet-truss lattice, (b) a unit-graded gyroid structure, (c) a face-centered cubic (FCC) hybrid hierarchical lattice, and (d) a 9 × 9 array of snake fang-inspired microneedles with a tip radius of 2.97 μm.(Adapted with permission from [27])

3. Conclusion

In the present study, the latest developments and challenges in 3D printing of porous-based microfluidic materials were discussed, aiming at introducing the current bottlenecks for further investigations. It was shown that recent advances in developing proper materials for 3D printing of glasses have enabled the commercially available 3D printing systems to fabricate glass structures. However, these advances have not been applied to porous-based microfluidic devices yet. The key challenge in printing microfluidic devices is their complex shapes, intricate details, and very small size of their structures. That's why open challenges still exist ahead of SLA or FDM printing of such materials in terms of the required resolution and implementation of technological facilities for fusion of glass materials that should be tackled in future studies.

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