A review on porous ceramics with hierarchical pore structure by 3D printing-based combined route

Yiran Man*, Guoqiang Ding*, Luo Xudong*, Kaihua Xue*, Dianli Qu* and Zhipeng Xie

*School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan, China; †State Key Lab of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing, China

ABSTRACT
In recent years, with the continuous progress of 3D printing technology, as well as the limitations of traditional preparation methods of porous ceramics, an increasing number of studies on the combination of traditional porous ceramic preparation methods and 3D printing technology for designing and preparing hierarchical porous ceramics with both macropores and micropores have been reported. This is an innovation in the design concept for the manufacturing of porous ceramics. This review focuses on the latest advances in porous ceramics prepared by combined methods, including traditional methods and 3D printing technology, and discusses the design concept and printing process of porous ceramics and the properties of porous ceramics. Case studies of different combination technologies are compared, and the technical features of the combined technologies are summarized. According to the success factors of existing combination technologies, the feasibility of combining traditional porous ceramic preparation methods with different 3D printing technologies is analyzed.

1. Introduction
With characteristics of low density, high specific strength, and excellent thermal properties [1–3], porous ceramics are extensively applied in applications such as filters, sensor arrays, catalyst carriers, medicine, thermal insulators, separation membranes, tissue-engineering scaffolds, lightweight construction materials, and so on [4–8]. Conventional processes for processing porous ceramics have existed for some time, including the pore forming agent method, polymer template replica methods, sol-gel method, foam-gelcasting, and freeze casting. These processes can be almost just used for preparing macroporous bulk ceramics with simple structures and shapes [9]. However, the disadvantages in the properties of porous products manufactured by these processes are gradually becoming realized. The foaming agent method has some limitations on the shape of products, so it is difficult to generate products with complex shapes [10,11]. The process of replica technique is that the cellular structures are prepared by impregnating synthetic templates such as polyurethane foams or natural cellular structures with a ceramic slurry, drying the slurry and burning the template, followed by a sintering process. The prepared structures have the same morphologies as the former templates. Due to the pyrolysis of the template, the ceramic struts are hollow, thus degrading the mechanical strength of the cellular structures [12,13]. The sol-gel process mainly uses colloidal particles in the gelation process, leaving small pores in gel processing and heat treatment to form a controllable porous structure. The sol-gel method has restrictions on raw materials and low production efficiency [14–16]. Meanwhile, the properties and applications are based on pore size, porosity, and pore size distribution of porous ceramics (shown in Figure 1). The design of compatible pores and complex structures, according to the environment, can improve the performance of porous ceramic products [17,18].

3D printing technology (also known as additive manufacturing technology) can also be used to prepare porous ceramics [19]. The 3D printing method involves directly designing the 3D structure of a porous ceramic body by a computer, preparing the porous body by 3D printing, and then completing the post processing of the green body according to different 3D printing technology requirements [20]. Actually, 3D printing technology is a general term for a series of technologies including direct ink writing (DIW), inkjet printing (IJP), and three-dimensional printing (3DP); technology of interlayer curing with light-sensitive materials such as stereolithography (SLA), digital light processing (DLP), and two-photon polymerization (TPP); technology of interlayer curing with laser sintering such as selective laser sintering...
(SLS) and selective laser melting (SLM) and technology of interlayer curing with hot melt such as laminated object manufacturing (LOM) and fused deposition modeling (FDM) [21–27]. Each technology has its own unique molding process, type of feedstock, and performance of products. Among them, some technologies are more commonly used to manufacture dense bulk, and others are more commonly used to fabricate porous grid structures. More details on the process flows and characteristics of 3D printing of ceramics can be found in a review by Chen et al. [28]. The 3D printing method adds degrees of freedom with respect to the design of porous ceramic products. This goes far beyond stochastically irregular foams or regular honeycombs and allows the manufacturing of porous ceramic products with tailored properties [29,30]. 3D printing enables the manufacturing of complex porous structures and features that may provide enhanced fixation stability through the design of three-dimensional structures compared to conventionally manufactured porous geometries [31,32]. A literature review by Hwa et al. comprehensively summarized porous ceramics prepared by various 3D printing technologies before 2016, including the 3D printing mechanism and process to fabricate porous ceramic parameters that can affect porous ceramics, as well as the application and future trend of ceramics [33]. Most of the cases introduced in this paper are porous ceramics with macroscale pores. However, since 2016, many studies on bimodal porous structure hierarchical porous ceramics prepared by combining 3D printing technology with traditional porous ceramic preparation methods have been reported. These combinations generate porous ceramics that concurrently possess both macro- and microporosity. It is beneficial to the design of macropores and micropores, respectively. Meanwhile, the porosity, specific surface area, and specific stiffness of porous ceramics are greatly improved [9]. At present, no one has summarized this combined technology, and this combined technology will have a positive impact on the design, preparation, and application of porous ceramics.

The traditional preparation methods of porous ceramics have the difficulty of shaping complex products, lower strength, low production efficiency and toxicity assessment. Some recent studies show that these problems can be solved by the combination of traditional porous ceramic preparation and 3D printing technology. Meanwhile, hierarchical porous ceramics containing macro and micro pores can be prepared. This technology can also control the size, porosity, uniformity and directivity of micro pores by referring to the traditional preparation methods of porous ceramics. These properties have a great influence on the application of porous ceramic products. Therefore, this review aims to discuss the state of the art with regard to the above-listed porous ceramics with hierarchical pore structure by 3D printing-based combined route. This paper summarizes the recently published cases about the combination of 3D printing technology and traditional preparation of porous ceramics and introduces, in detail, the raw materials, feedstock types, feedstock preparation methods, printing technology used, and performance characteristics. The conditions, influencing factors, and properties of the products of these combined methods are analyzed.

2. Adding ceramic hollow spheres (AHS)

Since the 2000s, adding ceramic hollow spheres (AHS) has been developed to prepare porous ceramics by replacing ordinary powder with hollow spherical material [34]. Porous silicon nitride ceramics and closed-cell alumina ceramics have been fabricated in this way [35,36]. In addition, most 3D printing ceramics directly use ceramic powder as feedstock or prepare ceramic ink, filaments, and green sheets from powder raw materials [28]. Therefore, hierarchical porous ceramics with bimodal pore structures can be manufactured by combining AHS and 3D printing. Both the size, shape, and distribution of macro- and micropores can be designed in this way.

2.1. In conjunction with selective laser sintering (SLS)

SLS technology is a process using heat produced by laser irradiation to solidify powder material [37]. Therefore, it is a new idea to use hollow spheres in SLS technology. Some studies on this method have also been reported. The team of An-Nan Chen has performed a series of in-depth studies in this field. In one of their studies, highly porous mullite ceramic foams were prepared by combining SLS and AHS as a novel method [38]. To build very complex-shaped porous ceramic products can be used as sensors, filters,
piezoelectric transducers, heat dissipaters, thermal insulators, commercially available fly ash hollow spheres FAHSs with an average diameter of 75.5 μm were used to prepare feedstock for SLS 3D printing. After calcination at 900°C for 1 h, FAHSs were mechanically mixed with polyamide-12 (PA12) as a sacrificial binder phase with a mass ratio of 9:1. Then, the prepared feedstock was used for an SLS process with a laser power of 6.6 W and preheating temperature of 145°C. After SLS, debinding and sintering were conducted separately. The detailed process is shown in Figure 2(a). Finally, after sintering at increasing temperatures from 1250°C to 1400°C, porous mullite ceramic foams were characterized with linear shrinkage from 2.7% to 14.4%, porosity from 88.7% to 79.9%, and the compressive strength from 0.2 MPa to 6.7 MPa, respectively. Within this range, an increase in sintering temperature can enhance the strength of porous mullite ceramics. Before this study, research on SLS technology focused on how to improve the density of ceramic parts, and there were few reports on the preparation of porous ceramics.

Although the team’s research has strengthened the link between SLS technology and porous ceramics, only porous ceramics with micropores have been prepared. On this basis, the team prepared hierarchical porous mullite ceramics with adjustable bimodal pore structures for the first time in a similar way [39]. In this study, calcined FAHSs and PA12 were mixed by mechanical mixing to prepare feedstock for SLS. Then, 3D printing, debinding, and sintering were performed in succession. The macroscopic morphology, micromorphology, and printing process are shown in Figure 2(b-d). The porosity of the material and products can be easily observed. The effects of PA12 addition of feedstock for SLS printing on porosity, pore size distribution, compressive strength, and thermal conductivity were investigated. With increasing PA12 content from 10% to 25%, the porosity of the porous ceramics increases, but the strength decreases. The total porosity firstly increased from 85.1% to 85.2%, and then obviously increased to 86.7%. The thermal conductivity of the lightweight ceramics was also relatively low which could be as low as 0.06 W/(m·K) due to the special pore structures formed from the FAHSs and SLS technique. When the porosity of porous ceramics reaches a maximum of 85.2 ± 0.4%, its strength reaches 2 MPa, which is higher than that of porous ceramics prepared by traditional methods. The design of pore structures and microstructures can enhance pore control and strength using ceramic hollow spheres as feedstock for SLS. This work also lays the foundation for the preparation of lightweight porous ceramics with adjustable bimodal pore structures. The printed porous ceramics can be widely used in applications such as thermal insulators, sound absorption materials, filters and catalyst supports [40,41]. In another study by their team, the enhancement mechanism of the compressive strength of porous mullite ceramics prepared by SLS using FAHSs as feedstock was investigated [42]. With the increase of sintering temperature from 1250°C to 1400°C, the average closed pore size of ceramic foam decreases from 58.7 mm to 46.0 mm, while the average open pore size distribution kept constant with average pore size of 32.9 mm. Consequently, the total porosity of mullite ceramic foams decreases from 89.1 ± 0.1% to 81.5 ± 0.6% mainly due to the reduction of enclosed hollow spaces of FAHSs. The compressive strength of ceramic foams shows the opposite tendency increasing from 0.12 ± 0.02 MPa to 4.86 ± 0.18 MPa. The study found that the liquid phase diffusion of K, Ca, and Ti can reinforce sintering necks between FAHSs and

![Figure 2](image-url)

**Figure 2.** (a) The detailed process of preparation of high-porosity mullite ceramic foams by combining SLS and AHS [27]; (b) Calcined fly ash hollow sphere [28]; (c) SEM image of calcined fly ash hollow sphere [28]; (d) Printing process using fly ash hollow sphere [29]; (e) The porous mullite ceramic with bimodal pore structures [30]; (f) Microstructure of the porous mullite ceramic [30].
improve the thickening and densification of sphere shell walls. The porous mullite ceramic with bimodal pore structures and its microstructure are shown in Figure 2 (e-f). It is helpful to design porous ceramics with high compressive strength and high porosity. This kind of highly porous mullite ceramics are desirable for a widespread industrial applications in thermal insulators, particle filters, catalyst supports, separation membranes, etc [43–46].

In addition, not only FAHSs, but also other hollow spheres can be used for preparing porous ceramics by SLS. Hollow alumina spheres are also used for SLS technology to prepare porous ceramics [47]. The preparation process of Al₂O₃ polyhollow microsphere (PHM) ceramics by SLS and the microstructure of the raw material and porous ceramics sintered at 1500°C, 1550°C, and 1650°C are exhibited in Figure 3(a–e), respectively. Similarly, Al₂O₃ PHMs and epoxy resin (E12) were mechanically mixed, and composite powders were used for feedstock of SLS. After 3D printing, debonding was performed according to the TG/DTA curve. Then, samples were sintered at different temperatures from 1500°C to 1650°C. As a result, with increasing sintering temperature, the pore size distribution did not change considerably, while the porosity of porous Al₂O₃ ceramics decreased from 77.09% to 72.41% and the mechanical performance of porous Al₂O₃ ceramics increased from 0.18 MPa to 0.72 MPa. Moreover, porous SiC ceramics were manufactured by adding SiO₂ hollow microspheres via SLS [34]. The designed pattern diagram of hierarchical porous ceramics with adjustable bimodal pore structures with both macropores and micropores is shown in Figure 3(f). The composite powders were composed of SiC, kaolin clay, Al₂O₃, E12, and SiO₂ hollow microspheres. In these ingredients, SiO₂ hollow microspheres were added as a pore forming agent similarly due to multifunctionalization. The effects of sintering temperature, size of SiO₂ hollow microspheres, and addition of SiO₂ hollow microspheres on the porosity and flexural strength of porous SiC ceramics were studied. It was found that the three-point bending strength of the porous SiC ceramics increased with increasing sintering temperature below the temperature at which SiC was overoxidized. As the content of SiO₂ hollow spheres increased, the microstructure of porous ceramics loosened. The increase in hollow spheres can increase the open porosity of porous ceramics. Finally, porous SiC preforms with a high porosity from 92% to 97% and high flexural strength from 33.13 to 61.93 Mpa were obtained. The micrographs of the microspheres can be found in Figure 3(g).

Research on the combination of AHS and SLS has a foundation on whether hollow spheres are used as pore wall structures or pore forming agents. This is closely related to the powder-based feedstock and molding process of SLS. With the enrichment of research and the improvement of the preparation

Figure 3. (a) Preparation process of the preparation of Al₂O₃ PHM ceramics [31]; (b) Microstructure of raw material [31]; (c) Microstructure of porous ceramics sintered at 1500°C [31]; (d) Microstructure of porous ceramics sintered at 1550°C [31]; (e) Microstructure of porous ceramics sintered at 1650°C [31]; (f) The designed pattern diagram of hierarchical porous ceramics [32]; (g) The micrographs of micro pore [32].
technology of hollow spheres, an increasing number of materials will be used to design and prepare porous ceramics with complex pore structures.

2.2. Discussion on combining AHS with other 3D printing technologies

AHS has been used in powder-based SLS technology due to the similar characteristics of hollow spheres and powders. The combination of AHS and other 3D printing technologies has not been reported often. Whether AHS can be used in other 3D printing technologies will be a subject of deep research.

As another powder-based 3D printing technology, in a process of three-dimensional printing (3DP), the three-dimensional structure is divided into several discrete structural units, and then the binder is selectively sprayed on the surface of the ceramic powder bed under computer control. To ensure that the binder can be extruded from the print head smoothly, the liquid content and rheological properties of the binder should be adjusted before use [17]. Therefore, it is expected that porous ceramics with complex pore structures can be prepared by the combination of hollow spheres on the powder bed and proper binder. Similarly, in SLA and DLP technology, the selection of photosensitive resin will also affect the application of hollow sphere materials in the 3D printing process.

As slurry-based or bulk solid-based 3D printing technology [17], direct ink writing (DIW), fused deposition modeling (FDM), and laminated object manufacturing (LOM) use slurry, filaments, or precursor sheets as feedstocks. The feedstock can be prepared by mixing hollow spheres with binders that are viscous at room temperature or after melting at high temperatures. Therefore, the combination of adding hollow sphere technology in 3D printing technology for the design and fabrication of porous ceramics with complex pore structures has broad prospects.

3. Foaming process

In a foaming process, air is injected into a suspension or liquid media, which is subsequently set to keep the structure of air bubbles formed. After sintering at high temperatures, the consolidated foams can turn to high-strength porous ceramics in most cases. The foaming process is an easy, cheap, and fast way to prepare macroporous ceramics with open or closed porosities from 40% to 97% [48]. Many scholars have successfully prepared hierarchical porous ceramics with complex pore structures by combining the foaming process with direct ink writing (DIW) [49–54].

The description of DIW involves manufacturing a designed three-dimensional structure by extrusion methods using a slurry with high viscosity and plasticity layer by layer at room temperature [55,56]. Recent studies combined the foaming process with DIW using foam inks instead of ordinary slurry to realize hierarchical porous structures in a DIW process. This combined technology was put forward by Muth J T et al. for the first time and was called “direct foam writing” [49]. In the study of Muth J T et al., butyric acid was used as a surfactant to prepare aqueous dispersions of alumina particles with a solid load of 35 vol % at pH < 3. Then, the aqueous suspension of partially hydrophobized alumina particles was foamed by mechanical frothing to prepare the foam ink for DIW printing. As high viscosity, storage modulus, and yield stress may impede aeration and affect the forming process, the viscosity, storage modulus, and yield stress of aqueous suspensions of foam ink made of partially hydrophobized alumina particles was studied and adjusted. Finally, they obtained colloidal gel possesses an apparent viscosity that is equivalent to the colloidal fluid at shear rates above 10−1 s−1, and the apparent viscosity of foam ink increases by an order of magnitude on foaming. After printing, the printed structures needed to control humidity for at least one week and dry for at least 24 h. The debinding and sintering process is set at 200°C, 300°C, 500°C, and 700°C for 20 hours, 1500°C for 3 hours, and increased from room temperature to 1500°C at a rate of 1°C/min.

The sintered samples and their microstructures are shown in Figure 4(a–c). Macropores and micropores can be easily observed. As a result, porous ceramics produced by this combined technology can obtain low relative density (~6%) and high specific stiffness (~107 Pa/(kg/m3)). The obtained cellular ceramics can be used for many applications, including lightweight structures, thermal insulation, tissue scaffolds, catalyst supports, and electrodes.

In addition to porous ceramics with bimodal pore structures, porous ceramics with three levels of pores have also been reported. In a study by Zhang X et al., porous ceramics with low density and hierarchically porous structures with tunable macropores and nanoscale pores in the cell wall were manufactured by combining the foaming process and direct ink writing (DIW) using boehmite gel foams as feedstock, which could obtain a specific surface area of 300–400 m2/g [50]. The preparation process of lightweight boehmite ceramic foams with hierarchical structures via DIW printing is shown in Figure 4(d). The suspension, which was uniformly dispersed by boehmite powder and deionized water, was mechanically stirred at 1000 rpm, and sodium dodecyl sulfate (SDS) solution was then added dropwise at the same time. Foams were prepared from the suspension by mechanical stirring at 2000 rpm for 10 min. After that, KOH solution was added little by little to heighten the pH of foams, which can lead to foam gelation. After drying in an environment of 25°C and 80% humidity and sintering, a 3D printed lattice ceramic with three levels of pores contained millimeter-scale pores designed by the 3D model, micron-scale pores
derived from the bubble template, and nanometer-scale pores on the cell wall. The three levels of pores are shown in Figure 4(e-g). The simplicity of such approach and establishment of 3D hierarchical porous structure put forward in this paper enables low-cost synthesis of outstanding multifunctional porous materials with considerable application potential in catalysis, separation, tissue engineering fields.

In addition to the above reports, porous ceramics with ultrahigh overall porosity of 95.3% and robust compressive strength of 2.5 MPa using Al2O3-MgO-SiO2 foams, porous TiO2 structures with porosity of up to 65% and compressive strength of 12–18 MPa and porous Al2O3 ceramics with high porosity of 94% have been prepared through this method by combining the foaming process with DIW 3D printing [51–54]. The two technologies have good compatibility, as long as printing inks for foaming modification and porous ceramics with high strength and high porosity can be designed and prepared in this way. However, in view of the characteristics of the liquid properties of foam ink, it is unlikely to be applied to other 3D printing technologies due to the types of feedstock.

4. Freeze drying method

The freeze-drying method is a new way to prepare porous ceramics. The process is to use water and other liquid base media to solidify at low temperature, then sublime in vacuum to form regular pores, and then heat treatment at high temperature to obtain porous ceramics [57]. This technology is also used as a post processing method for 3D printed green bodies to prepare porous ceramic complex layered structures that regularly pass through pores [58,59].

4.1. Combining with direct ink writing (DIW)

The freeze drying method and direct ink writing (DIW) were combined to fabricate porous alumina scaffolds with bimodal pore structures in the study of Moon Y W et al. [58]. Schematic diagrams of the preparation process for porous alumina scaffolds and the design of macropores and micropores are shown in Figure 5(a-b), respectively. Macropores were constructed through the deposition of frozen alumina/camphene filaments and staggered and aligned micropores were created by the
4.2. In conjunction with laminated object manufacturing (LOM)

The freeze-drying method has also been used to manufacture porous ceramics in an LOM process in order to prepare porous ceramics with complex shape and high uniformity and directivity [59]. Although macro pores have not been designed, the ice crystals in the green body are sublimated by freeze drying so that pores are formed at the micro level. The manufacturing steps of this study are displayed in Figure 6(a). Alumina powder, water, and carboxymethyl cellulose sodium were mixed to prepare a slurry for LOM printing. It is worth noting that since printing is carried out at −20°C, the solidification between layers depends on the melting and freezing of ice crystals on the slurry surface. When the printing process was complete, the printed body was freeze dried to obtain a porous structure. In this process, the freezing temperature gradient induces the vertical growth of lamellar ice crystals to improve the orientation and uniformity of the pore structure and the compression strength of the ceramic parts. Meanwhile, the effect of the alumina solid content in the slurry on the porosity and compressive strength of porous ceramics was also studied. Finally, porous ceramics with true porosities of approximately 58% and 44% and compressive strengths of approximately 17 MPa and 21 MPa were fabricated via LOM combined with layer-by-layer freezing technology using slurries with alumina contents of 50 wt.% and 60 wt.%, respectively. The porous ceramic processed by Zhang et al. and its microstructure are shown in Figure 6(b-c). Pores with uniform distribution and direction can be observed.

With the combination of the freeze-drying method and DIW and LOM, the controllability of the ice crystal structure in the porous ceramic structure is improved, and the uniformity and directivity of the layered pore structure are enhanced. In addition, a uniform structure can also improve the mechanical properties of porous ceramics. However, freeze drying technology is difficult to apply to other 3D printing technologies because other technologies have difficulty providing water and other liquid base media for freezing.

5. Others

5.1. Particle stacking combining with direct ink writing(DIW)

Particle stacking involves adding low-temperature sintering additives or superfine aggregates into large aggregates, which are easy to liquefy or sinter
at high temperatures by using sintering aids or fine aggregate materials to connect the aggregates together. The larger the particle size of the aggregate, the larger the average pore size of the porous ceramic, while the more uniform the particle size of the aggregate, the more uniform the pore
distribution and the smaller the pore size distribution. The particle packing method is simple, and the product’s strength is high [63].

A functional hierarchical porous TiO$_2$ lattice used as photocatalytic carrier with a high specific surface area of more than 14 m$^2$/g was fabricated by combining particle stacking and DIW technology [64]. The design mentality of bimodal pore structures is shown in Figure 7(a). In this study, macropores were formed by interweaving slurry lines in the printing process, and micropores were formed by stacking particles with different particle sizes during sintering. TiO$_2$ nanoparticles (=21 nm) and submicrometer particles (=0.1–0.5 μm) and an aqueous solution of Pluronic F127 were used to prepare inks with a porous structure with macropores and micropores and meet the requirements of DIW. After 3D printing, debinding, and sintering, a three-dimensional lattice was prepared. The printed green body, cross-sectional SEM images, and microstructure of the surface morphology are shown in Figure 7(b-d). After sintering at 600°C, 800°C and 900°C, the obtained scaffold maximum compressive strength of 0.082 Mpa, 0.129 Mpa and 5.36 MPa. Meanwhile, both macropores and micropores were observed to be consistent with the original design idea.

### 5.2. Sacrificial template combining with direct ink writing (DIW)

Sacrificial template method is widely used in the preparation of porous ceramics [65,66]. Similarly, this method can also be combined with 3D printing to produce porous ceramics with hierarchical pore structure [67]. A facile and controllable method for the fabrication of SiOC ceramic components with hierarchical porosity is reported in the work by Huang et al [68]. In this study, polymethylsiloxane(MK) and polymethyl methacrylate (PMMA) were mixed into inks for DIW as the preceramic precursor for SiOC and sacrificial templates for the generation of pores. For investigating the influence of the content and size of the PMMA particles, inks were prepared with microbeads of 0.46, 5, 10, 25 and 50 μm nominal size, and in an amount of 50, 60, 70, 80 vol% on the properties of SiOC ceramic components. The fabrication procedure of hierarchically porous SiOC scaffolds are shown in Figure 8. The ink is printed in 3D to form a ceramic body, which is then sintered at 1000°C. As a result, SiOC ceramics with high open porosity and total porosity of 85.8% and 87.8% are obtained when using 25 μm microbeads and 80% volume fraction. High compressive strength of $8.19 \pm 3.06$ MPa was obtained when using 0.46 μm microbeads. The possibility and compressive strength of manufacturing scaffolds possessing filaments with interconnected porosity and greatly increased geometric surface as well as enhanced compressive strength will prove beneficial for applications such as catalyst support, biomedical components, energy devices, etc.

### 5.3. Whisker coating combining with 3D printing

Whiskers-coated ceramic structures prepared by DLP 3D printing were proposed by Chen et al. for the first time to achieve effective and efficient oil/water separation in various situations. In this work, Aluminum borate whiskers (Al$_{13}$B$_4$O$_{33}$) were coated on printed alumina structures by an in situ growth method, acting as a functional surface with superhydrophilicity as well as underwater superoleophobicity. As a result, for free oil/water mixture, whiskers-coated honeycomb structure efficiently removed water with high flow rate and separation efficiency over 99% applied for different kinds of oil [69].

In the study of Wu et al., multilevel porous calcium phosphate (CaP) bioceramic orthopedic implants were constructed to mimic the micro/nanostructural hierarchy in natural wood by DIW 3D printing. The biomimetic hierarchical porous scaffolds were fabricated by combining three-dimensional (3D) printing technology...
Table 1. Porous ceramics prepared by combining route

| Reference Applications                                                                 | Compressive strength | Porosity or other characterization | Additives                  | 3D printing technology | Traditional preparation of porous ceramics | Raw material |
|---------------------------------------------------------------------------------------|----------------------|------------------------------------|---------------------------|------------------------|--------------------------------------------|--------------|
| Piezoelectric transducers, heat dissipaters, thermal insulators, particle filters,    | 0.2 to 6.7          | 79.9 to                            | Polyamide-12              | SLS                    | Adding ceramic hollow spheres (AHS)        | Fly ash hollow spheres (FAHSs) |
| catalyst supports, separation membranes, etc                                         | 2 MPa                | 85.2 ± 0.4                         | Epoxy resin (E12)        | Foaming process        |                                            | Al₂O₃ PHMs   |
|                                                                                        | 4.86 ± 0.18          | 89.1 ± 0.1%                        | Epoxy resin (E12)        |                        |                                            | Hollow SiO₂  |
|                                                                                        | 0.72 MPa             | 77.0%                              |                           |                        |                                            | Al₂O₃ particles |
|                                                                                        | -                    | 97%                                |                           |                        |                                            | Boehmite powder |
| Tissue scaffolds                                                                       | -                    | Relative density                   | Sodium dodecyl sulfate    | SLS                    |                                            | Al₂O₃, MgO, SiO₂ |
| Catalysis, separation                                                                  | -                    | (6%)                               | Sodium dodecyl sulfate    | Foaming process        |                                            | TiO₂ powder   |
| Lightweight structures                                                                 | 2.5 MPa              | Specific surface area of 300-400   | Polyvinyl alcohol         |                        |                                            | Al₂O₃         |
|                                                                                        | 12-18 MPa            | m²/g                               | Polyvinyl, alcohol propionic acid |                        |                                            | Al₂O₃         |
| Lightweight structures                                                                 | 8-16 Mpa             | 95.3%                              | Polyvinyl alcohol         |                        |                                            | Al₂O₃         |
| Biomedical scaffolds,                                                                  | -                    | 65%                                | Polyvinyl, alcohol        |                        |                                            | Al₂O₃         |
| Bone tissue                                                                            | -                    | 88 to 93%                          | Polyvinyl alcohol propionic acid |                        |                                            | Al₂O₃         |
|                                                                                       | -                    | 78.7%                              | Polyvinyl alcohol propionic acid |                        |                                            | Al₂O₃         |
and hydrothermal treatment. First-level macropores (~100 – 600 µm) and second-level micro/nanoscale pores (~100 – 10,000 nm) were obtained for promoting bone tissue ingrowth and promoting nutrient/metabolite transportation with high compressive strength of 2.92 MPa [70].

6. Summary

In recent years, with the continuous development of 3D printing technology and equipment and the almost sophisticated preparation mechanism of porous ceramics, an increasing number of porous ceramics with excellent performance have been designed and manufactured by combining 3D printing technology with traditional preparation methods of porous ceramics. In this review, several types of combination technology that can design macroholes and microholes at the same time were briefly introduced. The design concept and preparation process of the porous ceramics were described in detail, and the reported studies were discussed. The principles, traditional technology, 3D printing technology, feedstock preparation process, and additives used in each study are comprehensively compared in Table 1.

In general, the method of adding hollow spheres can design and control the micropore size of porous ceramics by using different sizes of hollow spheres. The micro pore size and distribution can be controlled by the hollow materials used. The porosity of porous ceramics prepared by this method combined with 3D printing technology can reach 97%. Porous ceramics prepared by this method are suitable for many fields, including piezoelectric transducers, heat dissipaters, thermal insulators, particle filters, catalyst supports, separation membranes, etc. At present, most of the research mainly focuses on the technology of combining adding hollow spheres with SLS. Because of its powder-like features, hollow spheres can be used as raw material in other powder-based, slurry-based, even bulk solid-based 3D printing technologies. However, this method requires additional attention in the formation of open and closed pores in porous ceramics. Porous ceramics with ultrahigh porosity up to 95.3%, low relative density of ~6%, high specific surface area of 300–400 m²/g can be prepared by the foaming method combined with 3D printing technology, respectively. At the same time, it is easier to control the formation of open and closed pores in porous ceramics prepared by foaming method. The strength of porous ceramics can be improved by designing macrogrid structures using 3D printing. However, due to the features of foam ink, it is not suitable to apply to powder-based 3D printing technology. It is worth noting that ceramic flakes prepared by foaming method may be used in bulk solid-based 3D printing technology. Open pores with uniform direction and distribution can be formed in porous ceramics by directional solidification of water-based media combined with DIW or LOM. Porous structure with locally tuned porosity and pore size can have mechanical functions and biological performances tailored to specific bone defects owing to perfect interconnections between the pores and uniformity. Although porous ceramics with high compressive strength up to 21 MPa can be prepared by freeze-drying, high porosity can not be obtained by this method. Similarly, the freeze-drying method is also difficult to combine with powder-based 3D printing technology. Porous ceramics are prepared by using particle stacking with different sizes of particles. It is easy to operate and widely used. This method can be used in most 3D printing technologies. The sacrificial template method can control the size and control of the internal pores of porous ceramics according to the size and shape of the selected template. Similarly, sacrificial template method is also suitable for most 3D printing technologies adding different templates to feedstock of each 3D printing technologies. The way of whisker coating combining with 3D printing can form pore on the surface of scaffold printed by any 3D technology. This kind of pore is very suitable for filtration and promote nutrient/metabolite transportation in bioceramic orthopedic implants.

In summary, the traditional porous ceramic preparation method can be combined with 3D printing technology to prepare porous ceramics with excellent performance and macropores and micropores has gradually developed. These kinds of porous ceramics with hierarchical pore structure preparing by combined route can show great advantages in the fields of Industry, biomedicine environment protection and so on. This kind of combined route may have a significant impact on the design and preparation of porous ceramics. However, at present, research on this kind of technology is not systematic, and there are still a large number of combinable technologies that have not been studied.

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ORCID

Luo Xudong http://orcid.org/0000-0003-4588-1756
Dianli Qu http://orcid.org/0000-0002-0312-1671

References

[1] Ohji T, Fukushima M. Macro-porous ceramics: processing and properties. J Int Mater Rev. 2012;57 (2):115–131.
[2] Sciamanna V, Nait-Alib B, Gonon M. Mechanical properties and thermal conductivity of porous alumina ceramics obtained from particle stabilized foams. Ceram Int. 2015;41(2):2599–2606.

[3] Ha J-H, Lee S, Choi JR, et al. Development of a carbon-coated reticulated porous alumina material with tailored structural properties for potential radar-absorption applications. Ceram Int. 2017;43(18):16924–16930.

[4] Mendes MAA, Goetze P, Talukdar P, et al. Measurement and simplified numerical prediction of effective thermal conductivity of open-cell ceramic foams at high temperature. Int J Heat Mass Tran. 2016;102:396–406.

[5] Farahani H, Wajiran R, Hamidon MN. Humidity sensors principle, mechanism, and fabrication technologies: a comprehensive review. Sensors. 2014;14(5):7881–7939.

[6] Cao J, Dong X, Li L, et al. Recycling of waste fly ash for production of porous mullite ceramic membrane supports with increased porosity. J Eur Ceram Soc. 2014;34(13):3181–3194.

[7] Akhtar F, Andersson L, Oggunwumi S, et al. Structuring adsorbents and catalysts by processing of porous powders. J Eur Ceram Soc. 2014;34(7):1643–1666.

[8] Murphy SV, Atala A. 3D bioprinting of tissues and organs. Nat Biotechnol. 2014;32(8):773–785.

[9] Maurath J, Willenbacher N. 3D printing of open-porous cellular ceramics with high specific strength. J Eur Ceram Soc. 2017;37(15):4833–4842.

[10] Studart AR, Gonzenbach UT, Tervoort E, et al. Processing routes to macroporous ceramics: a review. J Am Ceram Soc. 2006;89(6):1771–1789.

[11] Lascarceix M, Champion E, Chartier T. Shaping by microstereolithography and sintering of macro–micro-porous silicon substituted hydroxyapatite. J Eur Ceram Soc. 2016;36(4):1091–1101.

[12] Schelm K, Abreu Morales E, Scheffler M. Mechanical and surface-chemical properties of polymer derived ceramic replica foams. Materials. 2019;12(11):1870.

[13] Wu H, Cheng Y, Wei L, et al. Effect of the particle size and the debinding process on the density of alumina ceramics fabricated by 3D printing based on stereolithography. Ceram Int. 2016;42(15):17290–17294.

[14] Zhang Z, Feng J, Jiang Y, et al. Self-sacrificial salt templating: simple auxiliary control over the nanoporous structure of porous carbon monoliths prepared through the solvothermal route. Nanomaterials. 2018;8(4):255.

[15] Pelanconi M, Rezaei E, Ortona A. Cellular ceramic architectures produced by hybrid additive manufacturing: a review on the evolution of their design. J Ceram Soc Jpn. 2020;128(9):595–604.

[16] Okada K, Isobe T, Katsumata KI, et al. Porous ceramics mimicking nature-preparation and properties of microstructures with unidirectionally oriented pores. Sci Technol Adv Mat. 2011;12(6):64701.

[17] Potdar A, Protasova LN, Thomasen L, et al. Designed porous milli-scale reactors with enhanced interfacial mass transfer in two-phase flows. React Chem Eng. 2016;2(2):137–148.

[18] Smolin AY, Romanov NV, Konovalenko IS, et al. 3D simulation of dependence of mechanical properties of porous ceramics on porosity. Eng Fract Mech. 2014;130:53–64.

[19] Liu J, Yang H, Ren B, et al. Highly porous ZrO2 cellular ceramics with 3D network architecture. J Ceram Int. 2020;46(6):7149–7154.

[20] Hammel EC, Ighodaro OL-R, Okoli Ol. Processing and properties of advanced porous ceramics: an application based review. J Ceram Int. 2014;40(10):15351–15370.

[21] Cesaran I, Segalman R. Robocasting provides moldless fabrication from slurry deposition. Ceram Ind. 1998;148(4):94–100.

[22] Le HP. Progress and trends in ink-jet printing technology. J Imaging Sci Technol. 1998;42(1):49–62.

[23] Sachs EM, Haggerty JS, Cima MJ, et al. Three-dimensional printing techniques, Google Patents. 1993.

[24] Jacobs FP. Rapid prototyping & manufacturing: fundamentals of stereolithography. McGraw-Hill, New York: Society of Manufacturing Engineers; 1992.

[25] Allahverdi M, Danforth S, Jafari M, et al. Processing of advanced electroceramic components by fused deposition technique. J Eur Ceram Soc. 2001;21(10–11):1485–1490.

[26] Varadan VK, Jiang X, Varadan VV. Microstereolithography and other fabrication techniques for 3D MEMS. Hoboken, New Jersey: John Wiley & Sons Inc; 2001.

[27] Kunieda M, Nakagawa T. Manufacturing of laminated deep drawing dies by laser beam cutting. Adv Technol of Plast. 1984;1:520–525.

[28] Chen Z, Li Z, Li J, et al. 3D printing of ceramics: a review. J Eur Ceram Soc. 2019;39:661–687.

[29] Lehnhus D, Vesenjak M, Schampheleire S, et al. From stochastic foam to designed structure: balancing cost and performance of cellular materials. Materials. 2017;10(8):922.

[30] Bhatte D. Four questions in cellular material design. Materials. 2019;12(7):1060.

[31] Banerjee S, Kulesha G, Kester M, et al. Emerging technologies in arthroplasty: additive manufacturing. J Knee Surg. 2014;27(3):185–192.

[32] Fu Y, Chen Z, Xu G, et al. Preparation and stereolithography 3D printing of ultralight and ultralast ZrO2 porous ceramics. J Alloy Compd. 2019;789(15):867–873.

[33] Hwa LC, Rajoo S, Noor AM, et al. Recent advances in 3D printing of porous ceramics: a review. Curr Opin Solid St M. 2017;21(6):323–347.

[34] Sun X, Zeng T, Zhou Y, et al. 3D printing of porous SiC ceramics added with SiO2 hollow microspheres. Ceram Int. 2020;46(14):22797–22804.

[35] Shao Y, Jia D, Liu B. Characterization of porous silicon nitride ceramics by pressure less sintering using fly ash cenosphere as a pore-forming agent. J Eur Ceram Soc. 2009;29(8):1529–1534.

[36] Geng HT, Hu XX, Zhou YJ, et al. Fabrication and compressive properties of closed-cell alumina ceramics by binding hollow alumina spheres with high-temperature binder. Ceram Int. 2016;42(14):16071–16076.

[37] Kruth JP, Wang X, Laoui T, et al. Lasers and materials in selective laser sintering. Assembly Autom. 2003;23(4):357–371.

[38] Chen A, Li M, Xu J, et al. High-porosity mullite ceramic foams prepared by selective laser sintering using fly ash hollow spheres as raw materials. J Eur Ceram Soc. 2018;38(13):4553–4559.

[39] Meng L, Chen A, Xin L, et al. Lightweight mullite ceramics with controlled porosity and enhanced properties prepared by SLS using mechanical mixed FAHSS/polyamide12 composites. Ceram Int. 2019;45(16):20803–20809.
[40] She JH, Ohji T. Fabrication and characterization of highly porous mullite ceramics. Mater Chem Phys. 2003;80(3):610–614.

[41] Han L, Deng XG, Li FL, et al. Preparation of high strength porous mullite ceramics via combined foam-gelcasting and microwave heating. Ceram Int. 2018;44:14728–14734.

[42] Chen A, Meng L, Wu J, et al. Enhancement mechanism of mechanical performance of highly porous mullite ceramics with bimodal pore structures prepared by selective laser sintering. J Alloy Compd. 2019;776:486–494.

[43] Fukushima M, Yoshizawa Y. Fabrication of highly porous silica thermal insulators prepared by gelation-freezing route. J Am Ceram Soc. 2014;97(3):713–717.

[44] Liu Q, Xue T, Yang L, et al. Controllable synthesis of hierarchical porous mullite fiber network for gas filtration. J Eur Ceram Soc. 2016;36(7):1691–1697.

[45] Cao J, Dong X, Li L, et al. Recycling of waste fly ash for production of porous mullite ceramic membrane supports with increased porosity. J Eur Ceram Soc. 2014;34(13):3181–3194.

[46] Liu J, Dong Y, Dong X, et al. Feasible recycling of industrial waste coal fly ash for preparation of anorthite-cordierite based porous ceramic membrane supports with addition of dolomite. J Eur Ceram Soc. 2016;36(4):1059–1071.

[47] Liu S, Li M, Wu J, et al. Preparation of high-porosity Al2O3 ceramic foams via selective laser sintering of Al2O3 poly-hollow microspheres. Ceram Int. 2020;46(4):4240–4247.

[48] André RS, Gonzenbach UT, Tervoort E, et al. Processing routes to macroporous ceramics: a review. J Am Ceram Soc. 2006;89(6):1771–1789.

[49] Muth JT, Dixon PG, Woish L, et al. Architected cellular ceramics with tailored stiffness via direct foam writing. Proc Natl Acad Sci. 2017;114(8):1832–1837.

[50] Zhang X, Huo W, Liu J, et al. 3D printing boehmite gel foams into lightweight porous ceramics with hierarchical pore structure. J Eur Ceram Soc. 2020;40(3):930–934.

[51] Bo R, Liu J, Wang Y, et al. Hierarchical cellular scaffolds fabricated via direct foam writing using colloidal particle-stabilized foams as ink. J Am Ceram Soc. 2019;102(11):6498–6506.

[52] Aleni AH, Kretzschmar N, Jansson A, et al. 3D printing of dense and porous TiO2 structures. Ceram Int. 2020;46(10):16725–16732.

[53] Minas C, Carnelli D, Tervoort E, et al. 3D printing of emulsions and foams into hierarchical porous ceramics. Adv Mater. 2016;28(45):9993–9999.

[54] Chan S, Sesso ML, Franks GV. Direct ink writing of hierarchical porous alumina stabilized emulsions: rheology and printability. J Am Ceram Soc. 2020;103(10):5554–5566.

[55] Lewis JA, Smay JE, Stuecker J, et al. Direct ink writing of three-dimensional ceramic structures. J Am Ceram Soc. 2006;89(2):3599–3609.

[56] Lewis J. Direct ink writing of 3D functional materials. Adv Funct Mater. 2006;16(17):2193–2204.

[57] Deville S, Saiz E, Nalla RK, et al. Freezing as a path to build complex composites. Science. 2006;311(5760):515–518.

[58] Moon YW, Choi J, Hoh YH, et al. Porous alumina ceramic scaffolds with biomimetic macro/micro-porous structure using three-dimensional (3-D) ceramic/camphene-based extrusion. Ceram Int. 2015;41(9):12371–12377.

[59] Zhang G, Chen H, Yang S, et al. Frozen slurry-based laminated object manufacturing to fabricate porous ceramic with oriented lamellar structure. J Eur Ceram Soc. 2018;38(11):4014–4019.

[60] Moon YW, Shin KH, Koh YH, et al. Production of highly aligned porous alumina ceramics by extruding frozen alumina/camphene body. J Eur Ceram Soc. 2011;31(11):1945–1950.

[61] Salinas AJ, Esbrit P, Vallej-Regi M. A tissue engineering approach based on the use of bio ceramics for bone repair. Biomater Sci. 2013;1(1):40–51.

[62] Loh QL, Choong C. Three-dimensional scaffolds for tissue engineering applications: role of porosity and pore size. Tissue Eng B Rev. 2013;19:485–502.

[63] Liu D, Li Y, Lv C, et al. Permeating behaviour of porous SiC ceramics fabricated with different SiC particle sizes. Ceram Int. 2021;47(4):5610–5616.

[64] Xu C, Liu T, Guo W, et al. 3D printing of powder-based inks into functional hierarchical porous TiO2 materials. J Adv Eng Mater. 2020;22(3):1901088.

[65] Liu J, Li Y, Fan H, et al. Iron oxide-based nanotube arrays derived from sacrificial template-activated hydrolysis: large-area design and reversible Lithium storage. Chem Mater. 2010;22(1):212–217.

[66] Yan C, Xue D. Room temperature fabrication of hollow ZnS and ZnO architectures by a sacrificial template route. J Phys Chem B. 2006;110(14):7102–7106.

[67] Allison L, Menasce S, Bouville F, et al. 3D printing of sacrificial templates into hierarchical porous materials. Sci Rep. 2019;9(1). DOI:10.1038/s41598-018-36789-z.

[68] Huang K, Elsayed H, Franchin G, et al. 3D printing of polymer-derived SiOC with hierarchical and tunable porosity. Addit Manuf. 2020;36:101549.

[69] Chen Z, Zhang D, Peng E, et al. 3D-printed ceramic structures with in situ grown Whiskers for effective oil/water separation. Chem Eng J. 2019;373:1223–1232.

[70] Wu L, Zhou C, Zhang B, et al. Construction of biomimetic natural wood hierarchical porous-structure bioceramic with Micro/Nanowhisker coating to modulate cellular behavior and osteoinductive activity. ACS Appl Mater Interfaces. 2020;12(43):48395–48407.