3D printing of HAp/xSiO2 ceramic scaffolds for potential bone graft reconstruction

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Abstract. HAp has drawn great attention in recent years for its similarity to the inorganic component of bone and can be used as a biocompatible implant. However, the application is limited for its poor shape ability and low degradation ability. With the help of Digital Light Processing 3D printing technology, this study proposed a method for the fabrication of bone remodeling scaffolds with high complexity. In addition, this study found that the silica addition will help densify the HAp ceramic and make it transform to a more biodegradable TCP phase at low sintering temperature.

1. Introduction
According to the clinical report, bone implantation procedures in bone defective, ranging from a traffic accident to tumor or cancer therapy, is increasing 10% annually[1]. It is significantly critical to satisfying the growing need for bone remodeling therapy with the development of new bone repairing materials and fabrication technology[2]. The natural bone material, hydroxyapatite(HAp), has drawn great attention in recent years for its similarity to the inorganic component of bone and can be used as a biocompatible implant into the body where a biological bond will be formed together with bone tissue[3, 4].

Nevertheless, there are still some shortcomings in the clinical application of HAp. Among them, the biggest is that HAp is too stable in the body to be absorbed and replaced by new bones, which drastically restrict the bone conduction effect [5, 6]. The second is that the HAp has poor ability to shape complex geometry, which means conventional fabrication methods, like freeze-casting and gas foaming, cannot achieve the growing need for the clinical treatment of defects of large and complex[6]. The advent of three-dimensional(3D) printing is a promising approach to solve the problem by ceramics 3D printing technic[7]. 3D printing has made it possible to generate engineered preoperative bone defective shaped scaffolds through a computer-aided design (CAD) process with help of medical software. A variety of 3D printing technologies has been developed in the field of fabrication of tailored bone defect models, of which the widely used 3D printing technology is now extrusion-based 3D printing. However, the drawbacks of this method in bone repair modeling are its low accuracy and disability to fabricate hollow-
structured scaffolds[8, 9]. To address the problem, the digital light processing (DLP) based 3D printing method was proposed to fabricate customized 3D bone lattice models of high complexity and accuracy.

2. **Overall description of methods**

To make a full investigation of the mechanical properties of the porous structured ceramic scaffolds, a diamond macroscopic structure was used in this study. The lattice structure with a feature size of 5mm shown in figure 1 was built according to the diamond by replacing the atoms with cylindrical rods. The complete procedure of this study was divided into the generation of the diamond structure, the synthesis of preceramic slurry, the 3D printing and heat treatment process, and characterization of the scaffolds.

![Figure 1. Schematic of the method.](image)

2.1. **Generation of the diamond CAD structure**

The diamond porous macrostructure with a unit size of 5mm was used in this study. The CAD model of the structure was set to 70% of overall porosity to mimicking the trabecular bone. The rod-like structure was set to 1.5mm. The latticed structure was plotted within a 20×20×20mm³ cube, then transformed to Standard Triangle Language (STL) file[10] for the next fabrication process.

2.2. **Synthesis of preceramic slurry**

Rod-like HAp particle of size 30nm and silica powder with a particle size of 5μm was used as basic solid content. The HAp and silica powders were together mixed with a UV curable resin 10wt% per step until to the target amount. The absorption wavelength of the UV curable resin was 405nm, which is corresponding to the emission wavelength of the 3D printer used in this research. The resin used consisted of SR454NS Acrylic, Ethyl 4-(Dimethylamino) benzoate, and Triethanolamine. In order to ensure the slurry printable and avoid precipitation with long time storage, 2wt% polyethylene glycol (PEG-600, Aladin Inc., Shanghai, China) was added as dispersant and 3wt% 1,5-pentanediol (Aladin Inc., Shanghai, China) was added as the solvent. To fully mix the slurry, it was ball-milled in zirconia for 10h and then degassed in vacuum to let the gas fully exhaust. Following the above schedule, the SiO₂: HAp at weight ratios of 0%, 2%, 5%, and 10% were prepared to evaluate the influence of silica addition on mechanical properties.

2.3. **3D printing and heat treatment process**

It is vital that the ceramic scaffolds with high accuracy. To achieve this, the 3D printing settings were set to 25μm of layer thickness, 60s of initial layer exposure time and 6s for normal layers. The exposure time of the initial layers was set longer to make it adhere tightly to the printer (Jenny, Hangzhou, China) substrate. After done setting the printing parameters, the designed lattice structure saved as STL file was imported to the printer and then sliced. After printing finished, the green parts were removed from the substrate and preparing for the cleaning procedure. The cleaning procedure was first done by ultrasonic vibration in alcohol followed by high-pressure gas blowing to remove the residual slurry in the green body.
Heat treatment for the ceramic green body is also of great importance to maintain high density and structure integrity because the major mass in the green body is still organic. For the first heat treatment process, namely debinding, where decomposition of the organic happens intensely and gas evaporation drastically, the preceramic green body could possibly crack under high heat ratio with rapid temperature growth. To determine the optimized heat treatment process, the thermogravimetry-differential scanning calorimetry (TG-DSC) analysis was done for the green body in air condition, which was shown in Figure 2. According to the results of the TG-DSC, the debinding process was performed in a tube furnace (GSL-1400X, KJ Group, China).

![TG/DSC curve of the green body in air atmosphere.](image)

2.4. Characterization of the scaffolds

Potential phase change characterization was performed by X-ray diffraction (XRD, D8 Advance, BRUKER, Germany). The micro-computed tomography (μCT) was used to observe the internal topology of the sintered ceramic composite and get the 3D reconstructed model which can be used to evaluate the shrinkage. The surface morphology of granules was observed by scanning electron microscope (SEM) (Quanta 200, FEI, Netherlands). Gold-coating was performed for 90s to get the surface of the ceramic conductive. The diamond-latticed cubic scaffolds were fabricated to perform compressive strength tests by using a universal testing machine (Z330E, Zwick Roell, Germany) for mechanical properties. Five samples of each group were used for statistic reliability and the mean value was calculated.

3. Result analysis

3.1. Heat treatment analysis

The TG/DSC curve in Figure 2 was used to guide the debinding and sintering process. It can be seen that the weight of the green scaffold hardly changed from temperature 25°C to 300°C. The endotherm peak at about 400°C indicated a strongly endothermic reaction had occurred. This is the stage where the photosensitive resin volatilizes, and the mass loss drastically. When the temperature reaches 600°C, the weight of the green sample remained almost unchanged, illustrated that the resin and other binding elements had been completely removed. Based on the above analysis, the ceramic green body should be
fired at a low temperature below 600°C with a slow temperature increase rate of 0.4°C/min in vacuum atmosphere to completely remove the resin and then sintered into a ceramic at a higher temperature of 1200°C in air. The entire debinding and sintering process is carried out according to the following schedule (as shown in figure 3). For debinding process(figure 3a), set the heating temperature to 100°C and keep it for 0.5h, and then heat to 300°C at 1°C/min. Next, it was fired at 600°C at a temperature increase rate of 0.5°C/min and kept for 2h. For the sintering process(figure 3b), the furnace was heated to 1200°C in 2 hours and kept for 2 hours in the air atmosphere. In the first step, the cooling stage should be kept at 2°C/min to 900°C, and in the second step, it should be kept at 5°C/min to room temperature to avoid cracks.

Figure 3. The debinding and sintering parameters.

3.2. XRD analysis of the ceramic phase
For the purpose to investigate the phase transition of HAp with different silica addition during sintering, XRD patterns of different samples were performed after sintering. Figure 4(a) shows the XRD patterns of the pure HAp and silica added as-sintered samples. The result revealed that the pure HAp produced a diffraction pattern that was highly consistent with that of standard synthesized HAp. However, with the addition of silica, the phase transformed from typical HAp to TCP, and the trend was more apparent with the increasing addition of silica. According to the XRD analysis, the TCP phase is most likely to be α-TCP, for all the peaks match those of typical α-TCP. Moreover, with the addition of silica, the full width at half maximum (FWHM) decreased respectively, exhibited narrower peaks and higher peak intensity, which demonstrated that the sintered composite ceramics with increasing content of silica promote the crystalline of the composite and growth of crystal particles (figure 4, b-e).
3.3. Morphology characterization

It is significantly critical that the actual size in dimension and pore size of the sintered scaffolds within a controllable range for bone reconstruction compatibility. Therefore, the macroscopic and microscopic morphologies of the scaffolds green body were observed. As showed in figure 5, the unsintered green body had a pore size of 1mm. Lattice structure layered structure can hardly be seen with the process of the layer thickness of 25μm(figure 5b). Little residual powder still remained on the surface of the green body(figure 5c), which can be seen in the top view. It was also found that the printed green body was slightly larger than the designed model. This might result from the long exposure time of each layer and scattering of the preceramic slurry.

The micromorphology of the sintered ceramic composite is shown in figure 4b-e. From figure 4b to 4e, corresponding to the HAp, HAp with 2% silica, HAp with 5% silica, and HAp with 10% silica addition, it can be concluded that with increasing addition of silica, the micropores of the sintered ceramic became less and smaller. And the above phenomenon in turn had an influence on the macro size of the ceramic scaffolds. From the measurement of size and calculation of shrinkage of the sintered group, as is shown in Table 1, the silica added group showed greater shrinkage than the pure HAp group, which was consistent with the micromorphology shown in figure 4b-4e.
Table 1. Shrinkage of green body after sintering on three axes.

| Scaffolds | CAD model(mm) | Green body(mm) | AS-sintered(mm) | Shrinkage(%) |
|-----------|---------------|----------------|----------------|--------------|
|           | xy | z   | xy | z   | xy | z   | xy | z   |
| HAP       | 20.00 | 20.00 | 20.02 | 20.32 | 13.20 | 12.92 | 0.34 | 0.36 |
| 2%+HAP    | 20.00 | 20.00 | 20.06 | 20.48 | 12.75 | 12.24 | 0.36 | 0.40 |
| 5%+HAP    | 20.00 | 20.00 | 20.11 | 20.40 | 12.86 | 11.61 | 0.36 | 0.43 |
| 10%+HAP   | 20.00 | 20.00 | 20.02 | 20.81 | 13.17 | 12.64 | 0.34 | 0.39 |

4. Conclusion
The DLP-based 3D printing method for fabrication 3D bone mimicking diamond lattice of customized shape with high complexity was proposed in this study. The high porosity (70%) structure with tunable densification ceramic was obtained. The addition of silica will help densify the HAp ceramic and make it transform to TCP phase at low sintering temperature.

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