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Detailed structure of a new bioactive glass composition for the design of bone repair materials

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ABSTRACT

Detailed structure of a new bioactive glass composition (PSC, 54 mol% SiO₂, 35 mol% CaO and 11 mol% P₂O₅) was studied, and conventional glasses (45S5 and S70C30) were used as comparison. The structure information were obtained by HEXRD and solid NMR techniques. It was found that all the samples have different silicon and phosphorous coordination environment, there is Si-O-P network formed for PSC samples but not for 45S5 and S70C30 samples. These results may hopefully advance the design of new bioactive glasses.

1. Introduction

The life expectancy of the world population increased dramatically every year because of the developments of people's life. Plenty of bone implants are needed to maintain their quality of life after accidents or illnesses. However, current implants, e.g. metals and polymers, were biological inert triggering fibrous encapsulation after implantation and leading to a high rate of failure in the long time [1]. In order to avoid the flaw of bone implants, material scientists have been making great effort to develop synthetic bone materials. Among them, bioactive glasses (silicate-based glasses, phosphate-based glasses, borate-based glasses and borosilicate glasses) have provided many encouraging results [2–7].

The first silicate-based bioactive glass (Bioglass®) were reported by Hench, which has a composition known as 45S5 corresponding to 45 wt% SiO₂, 24.5 wt% Na₂O, 24.5 wt% CaO, and 6 wt% P₂O₅, and has been widely used in clinical, e.g. dental and orthopaedic fields [8,9]. However, these glasses need to be processed at very high temperatures. Sol-gel bioactive glasses processed at lower temperature were then explored. It was found that the gel-derived glasses had high surface area, porosity, and wider range of bioactive compositions (58S, 77S and S70C30, et al.), exhibiting higher bone bonding rates [10]. However, all these silicate-based glasses degrade slowly and usually take 1 to 2 years to disappear from the body [11].

Phosphate-based glasses (CaO-Na₂O-P₂O₅) have unique dissolution properties in body fluids, the degradation rates can be controlled from hours to several weeks by changing the glass composition. Furthermore,

these glasses can be synthesized as particles, fibres and microtubes to include different dopants that are able to induce a specific biological function and enhance biocompatibility in soft tissue [3]. However, these glasses didn't not embody good bioactivity for bone regeneration. Because of these limitations, it is necessary to search for new bioactive glasses compositions for the repair of bone defects.

Since the silicate-based glasses with lower phosphate content (< 5 mol%) have higher bioactivity for bone defects, whereas phosphate glasses without silicate content have higher degradation rates, it may be possible to prepare a new phosphosilicate bioactive glass with higher phosphate content accelerating the degradation rates for bone defects. In previously, we used a non-toxic phytic acid as phosphorous precursor to prepare CaO-SiO₂-P₂O₅ glasses by sol-gel process, it was found that a much broader range of bioactive composition were obtained especially at high phosphate content [12]. In which, the composition of (CaO)_{0.35}(SiO₂)_{0.54}(P₂O₅)_{0.11} (48.2 wt% SiO₂, 29.1 wt% CaO and 22.7 wt% P₂O₅, termed as PSC) has the best bioactivity, and the phosphate content is dramatically increased compared with conventional bioactive glasses. The PSC have also be found to have better cell proliferation, mRNA expression and osteocalcin and mineralization of hDPCs comparing with conventional 45S5 [13], and the released Si and P ions from PSC were larger than those released from 45S5, implying the higher degradation rate for PSC.

Detailed structural knowledge is a prerequisite for optimizing glasses design. The atomic-scale structure of bioactive glasses and its effect on bioactivity and chemical durability has attracted much attention, because of which is important to model and predict the

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behavior of bioactive glasses, and ultimately improve their design [14–17]. In this paper, the detailed structure of this new bioactive glass composition (PSC) with higher phosphate content was studied by HEXRD and NMR techniques, which are possible to gain detailed insight into its structure. The linking between phosphate and silicate structural units will be answered, hopefully advancing the design of new bioactive glasses.

2. Experimental

2.1. Sample preparation

Tetraethyl orthosilicate (TEOS, $\geq 99.0\%$) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co., Ltd. Phytic acid (50 wt% aqueous solution) was purchased from Sigma Aldrich. All the precursors were used without further purification in the sol-gel preparation.

Bioactive glass (PSC: SiO_2 -54 mol%, CaO -35 mol%, P_2O_5 -11 mol%) was prepared as previously reported [12]. Phytic acid (1.6 mL) was firstly added in the mixture of ethanol and water at room temperature, then TEOS (5.82 mL) was added through a syringe during stirring. After 1 h, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ powder (3.98 g) was added until a transparent solution formed (the sol), which was sealed in polypropylene containers and left to gel. The resultant gel was aged at 60 °C for one week and then at 120 °C for another two weeks, and then stabilized at 200 °C, 400 °C and 600 °C for 1 h to get PSC glasses. The stabilized PSC glasses were then grounded into powders for testing.

Bioactive glasses 45S5 (Bioglas®: SiO_2 -46.1 mol%, CaO -26.9 mol%, P_2O_5 -2.6 mol%, Na_2O -24.4 mol%) and S70C30 (SiO_2 -70 mol%, CaO -30 mol%), which have little or no phosphate content, were used as comparison. 45S5 glass was purchased from Schott. Bioactive glass S70C30 was prepared as previously reported [18]: TEOS (20 mL) was hydrolyzed in the mixture of ethanol and water for 30 min at room temperature with 2 N HNO_3 as catalyst. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (9.06 g) was added gradually under continuous stirring. The molar ratio of water to TEOS was 12:1. The obtained clear sol solution was sealed in a polypropylene container and left to gel. The gel was aged at 60 °C for a week, followed by drying at 120 °C for another week and then stabilized at 600 °C for 1 h to obtain the S70C30 glass. The stabilized S70C30 glasses were then grounded into powders for testing.

2.2. Thermogravimetric analysis (TGA-DSC)

Thermal gravimetric behaviors of the PSC gels were measured on a TA Q-600 instrument. The samples (around 5 mg each) were placed in alumina crucibles and measured under nitrogen flow at $20 \text{ mL} \cdot \text{min}^{-1}$. Data were collected from 50 °C to 800 °C at a heating rate of $5^\circ \text{C} \cdot \text{min}^{-1}$.

2.3. X-ray diffraction (XRD)

XRD measurements were performed on a Rigaku (D/MAX 2500) instrument with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), operated at 40 kV and 200 mA. The data were collected for 2θ values between 5 and 70° with a step size of 0.02°.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR were collected in the range 4000–400 cm^{-1} on a Bruker Einox 55 instrument. All samples were diluted with dry KBr, ground down to fine powders and pressed into pellets. Measurements were made at ambient temperature.

2.5. Bioactivity test and dissolution profile measurement

150 mg of PSC glass powders were immersed in 100 mL SBF at

$36.5 \pm 0.5^\circ \text{C}$ [19–22]; each sample was measured in triplicate. After immersing in SBF for 1 d, the powders were washed gently with pure water and left to dry in a desiccator without heating. Apatite formation was evaluated using FTIR and XRD.

2.6. Textural characterization

Pore texture of the PSC, S70C30 and 45S5 glass powders were analyzed using ASAP 2020 apparatus. The samples were degassed in vacuum oven at 200 °C for 10 h for the removal of moisture from the pores and then analyzed with nitrogen adsorption to determine the BET specific surface area (SSA).

2.7. Higher energy X-ray diffraction (HEXRD)

The atomic structure of the PSC, 45S5 and S70C30 glasses were characterized by HEXRD. The data were collected on BL13W1 in Shanghai Synchrotron Radiation Facility. The finely powdered glasses were enclosed inside a 2 mm thick circular metal annulus sealed on both sides by kapton film and mounted onto a flat-plate “ θ : 2θ ” instrumental set-up. X-ray energy is 69.525 keV ($\lambda = 0.1783 \text{ \AA}$). The data was normalized against the incident beam intensity and corrected for the background scattering using the empty cell, and for sample absorption, polarization of the incident beam, inelasticity (Compton scattering), scattering volume and sample self-scattering. The resulting structure factor, $S(Q)$, is Fourier transformed to obtain the total correlation function, $T(r)$, in real space [23,24]. Structural information was obtained from the diffraction data by modelling the r -space data using NXFIT software to compare with the experimental total correlation function. The structural parameters used to generate the r -space simulation are varied to optimize the fit to the experimental data. The uncertainties of HEXRD fitting data arise mainly from the fitting process and the overlapping pair correlation shells.

2.8. Solid state NMR

The magic angle spinning (MAS) solid state Nuclear Magnetic Resonance (NMR) measurements of 45S5, S70C30 and PSC powders were carried out by an AVANCE III 400 MHz instrument providing ^{31}P and ^{29}Si Larmor frequency of 161.58 MHz and 79.3 MHz, respectively. 4 mm MAS BB probes spinning at 12 kHz were used. For ^{31}P NMR, a 2 μs ($\sim 90^\circ$ tip angle) pulse was used, and the recycle delay was 1 s. For ^{29}Si NMR, a 2.0 μs pulse ($\sim 90^\circ$ tip angle) was used, and the recycle delay was 2 s. ^{31}P and ^{29}Si NMR spectra were referenced using $\text{NH}_4\text{H}_2\text{PO}_4$ ($\delta_{\text{P}} = 0.9$ ppm with respect to phosphoric acid) and tetramethylsilane ($\delta_{\text{Si}} = 0$ ppm), respectively.

3. Results

3.1. TGA-DSC analysis

Fig. 1 shows TGA-DSC traces of representative PSC gels after dried at 120 °C. Three stages of weight loss are observed: the first one occur between 180 °C and 200 °C with an exothermic peak, which may be associated with the removal of trapped solvent (water, ethanol and nitrate etc.); the second one occur between 200 °C and 400 °C, which may because the further removal of nitrate and the loss of organic moieties by further condensation; the third stage of weight loss commence from the end of second weight loss ($\sim 400^\circ \text{C}$) up to $\sim 600^\circ \text{C}$, which is most likely due to the further loss of organic moieties. In general, the dried gels show weight losses around 30% over the temperature range 50–800 °C during the course of TGA-DSC measurements. The end temperature of every stage is chosen as stabilization temperature for PSC glass, i.e. 200 °C, 400 °C and 600 °C.

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