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The Effect of Surfactant on the Properties of Nano Bioactive Glass

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Abstract: Bioactive glass is used as both bone filler and as a coating on implants and has been proved to bond to hard and soft tissues by the formation of surface hydroxyl carbonate apatite layer. Nano bioactive glass was prepared by sol-gel process. As new modification, Hydroxypropyl cellulose was added as a surfactant to investigate its effect on the properties of bioglass samples and subsequently more homogeneous nano bioactive glass with smaller particle size was obtained. Surface electron microscope (SEM) was used to examine the size, morphology and homogeneity of samples. X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analysis were also applied to evaluate the crystalinity and composition of bioactive powders.

Key words: Sol gel processing · Bioactive · Nano bioglass · Hydroxypropyl cellulose

INTRODUCTION

Bone regeneration is required in many clinical issues addressed by orthopedic and dental medicine. The autogeneous bone graft is the gold standard, but host tissue is often scarce and can hardly be modeled to the shape required for successful reconstruction. Then people's attention was transferred to implantation [1]. In 1969, Hench and co-workers established a specific compositional range of soda lime phosphosilicate glasses that did not become surrounded by fibrous tissue when implanted and, instead, could become intimately bonded to bone. This bone-bonding, melt-derived glass was trademarked Bioglass known as 45S5 bioactive glass [2-4].

The basic components of bioactive glasses are oxides of calcium, phosphorus and silicon in proportions that provide the material with surface activity [5]. The silica and phosphate compositions of this glass are within the range that allows dissolution and calcium phosphate formation at the surface, while maintaining an appropriate rate of degradability [6, 7]. In vitro, bone cells grow well on bioactive glass and bone matrix production appears to be enhanced when compared with growth on inert glasses or plastics [8, 9]. The effects of bioactive glass on bone cells has been shown to be both substrate [10] and solution mediated [11, 12]. In addition, bioactive glass is the only one, which could bond to hard and soft tissue [13].

Bioactive glasses can be formed either from the traditional melt-quenching or by the modern sol-gel method [14]. Sol-gel processing, an alternative to traditional melt processing of glasses, involves the synthesis of a solution (sol), typically composed of metal organic and metal salt precursors followed by the formation of a gel by chemical reaction or aggregation and lastly thermal treatment for drying, organic removal and sometimes crystallization [15]. This technology is a low temperature preparation method and the glasses prepared by sol–gel method may have porous structure with high specific surface area [16].

Cellulose and its derivatives have already been utilized in wide medical and pharmaceutical fields [17-20]. Among the derivatives, hydroxypropyl cellulose (HPC) is particularly used in the application fields [21-23] due to many advantages such as excellent film forming properties, biodegradability, biocompatibility etc [24-25]. The objective of the present study is to synthesize SiO_2-CaO- P_2O_5 bioactive glass system through sol-gel synthesis which is modified by incorporation of surfactant. The surfactant is known to influence particle size, size distribution, morphology and homogeneity. HPC was used as a surfactant to investigate its effect on bioactive glass properties.

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MATERIALS AND METHODS

Reagents and Standard Solutions: The composition studied was bioactive glass 58S (58 % SiO_2-33 % CaO-9% P_2O_5, based on mol %). The sol-gel precursors used in this study were Tetraethyl orthosilicate (TEOS), Triethyl phosphate (TEP), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \bullet 4H_2O$), distilled water, 1 M ammonia, 2 M nitric acid (Merck, Germany) and hydroxypropyl cellulose (HPC) (Aldrich, China). No additional purification was done on materials.

Nano Bioactive Glass Preparation: The initial procedure involved mixing TEOS, distilled water and HNO_3 in order. Ethanol as an alcoholic media was added to solution and allowed to react for 30 min for the acid hydrolysis of TEOS to proceed almost to completion. The following reagents were added in sequence allowing 20 min for each reagent to react completely: TEP, $Ca(NO_3)_2 \bullet 4H_2O$, ammonia solution. After the final addition, mixing was continued until the gel was formed. The gel was kept in the oven and heated at 70°C for one day to remove the residual water and ethanol. During about 3 hours the temperature was raised to 600°C slowly and then was calcined for 2 additional hours at 600°C to stabilize the glass and eliminate residual nitrate (sample BG-H0).

Modification in the Synthesizing Method by Adding Surfactant: Hydroxypropyl cellulose as a surfactant was dissolved in distilled water and stirred at room temperature for 1 day to become homogeneous mixture and then was used instead of distilled water in sol-gel bioactive glass preparation method. The concentration of HPC was 3, 6 and 9 grams per 1 liter of final solution. Following materials were added in the same order (sample BG-H3, BG-H6, BG-H9).

Characterization: The crystal structure and the phase present in resulting powders were analyzed with X-ray diffraction (XRD). This instrument (Philips PW 3710) works with voltage and current settings of 30 kV and 35 mA, respectively and uses Cu–Kα radiation (1.540510 Å). For qualitative analysis, XRD diagrams were recorded in the interval $20° \le 2\theta \le 50°$ at scan speed of 2° /min. The mean crystallite sizes "D" were determined according to the Scherrer equation ($D=0.9\lambda/\beta \cos\theta$, where λ is the X-ray wavelength (1.5405 Å), β is the full width at half maximum of the diffraction line and è is the diffraction angle).

The functional group analysis was performed by Fourier Transform Infrared Spectroscopy (FT-IR). The measurements were carried out in the transmission mode in the mid-infrared range (400–4000 cm^{-1}). Scanning electron microscopy (SEM XL30) was used to characterize the morphology and grain size of nano bioactive glass powders. The samples were coated with gold before the examination.

RESULTS AND DISCUSSION

The XRD result of calcified sample BG-H0 can be seen in Fig. 1. As you can see in this figure, the pattern confirms the formation of the bioactive glass nano powder with approximately amorphous structure. It can be detected that β-TCP and wollastonite (pseudowollastonite, JCPDS No. 19-0248) are the main phases in the bioglass samples. Pseudowollastonite is a bioactive ceramic material that induces direct bone growth [26, 27]. The calculation of the crystallite size from specimens is shown in Table 1. It can be seen that with incorporation of HPC into specimens' structure, crystallites size markedly has been decreased. FT-IR spectrum of sample BG-H0 was presented in Fig. 2. Two broad and strong absorption bands at 1082 and 3435 cm^{-1} could be ascribed to stretch vibration of Si–O–Si and O–H bond, respectively. The small band appeared at about 800 cm^{-1} was the typical absorption band of symmetric stretch vibration of Si–O, while the absorption band at 470 cm^{-1} was attributed to bending vibration of Si–O. A dispersive band that arose from the bending vibration of amorphous P–O appeared in the vicinity of 575 cm^{-1} [28, 29]. The peak at 1480 cm^{-1} due to bioglass particles mineralization in the atmosphere with some water and carbon dioxide were attributed to the presence of C–O bond [30] and the one at 884 cm^{-1} was related to carbonate groups [31-32].

SEM images of produced bioactive glass powders that could be used for study of the size, morphology and homogeneity of samples are shown in Figs. 3 and 4. Comparing these SEM figures, it is clearly seen that bioactive glass prepared by adding surfactant has smaller size, more homogeneous and more spherical particles.

Table 1: The crystallite size due to content of HPC

Content of HPC	Crystallite size (nm)
0	60
3	54
6	48
9	38

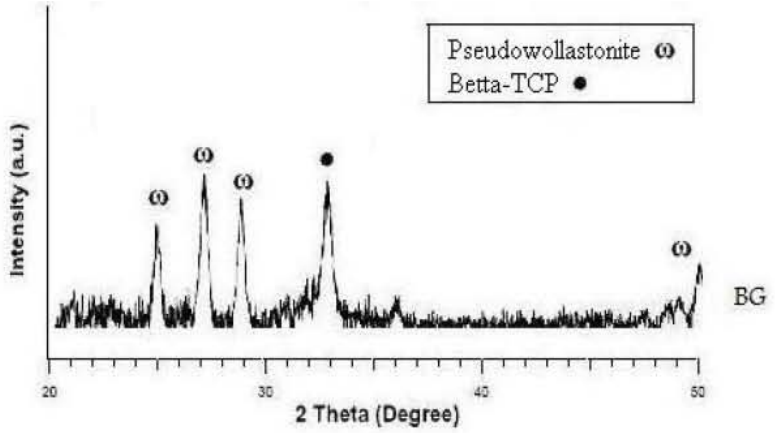

Fig. 1: XRD pattern of sample BG-H0

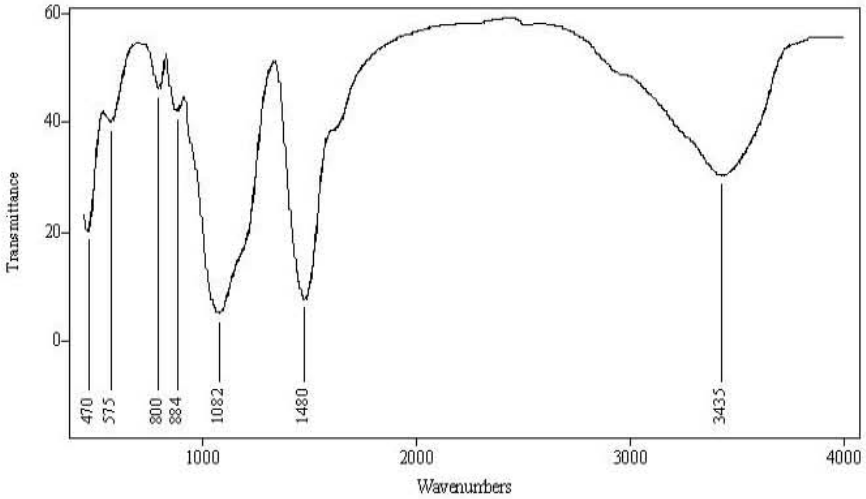

Fig. 2: FTIR spectrum of sample BG-H0

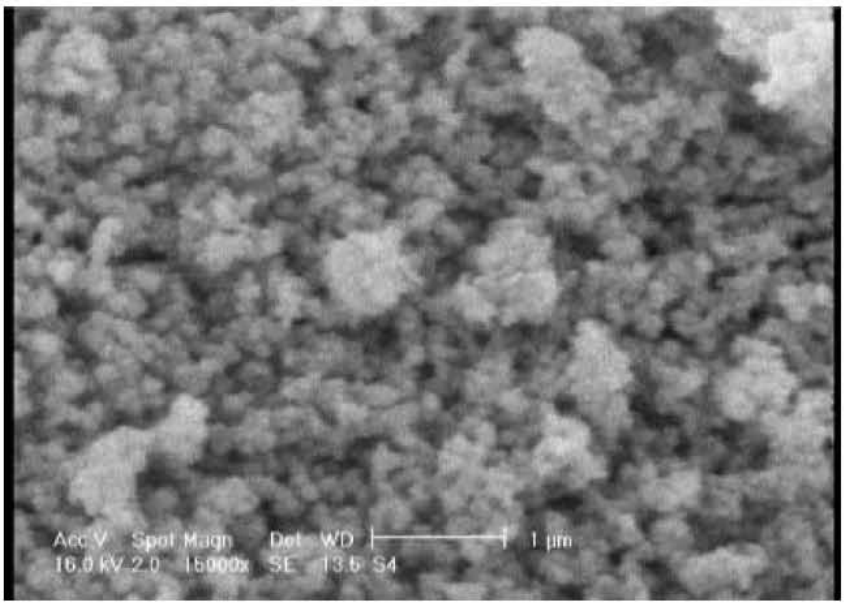

Fig. 3: SEM picture of sample BG-H0 (no HPC)

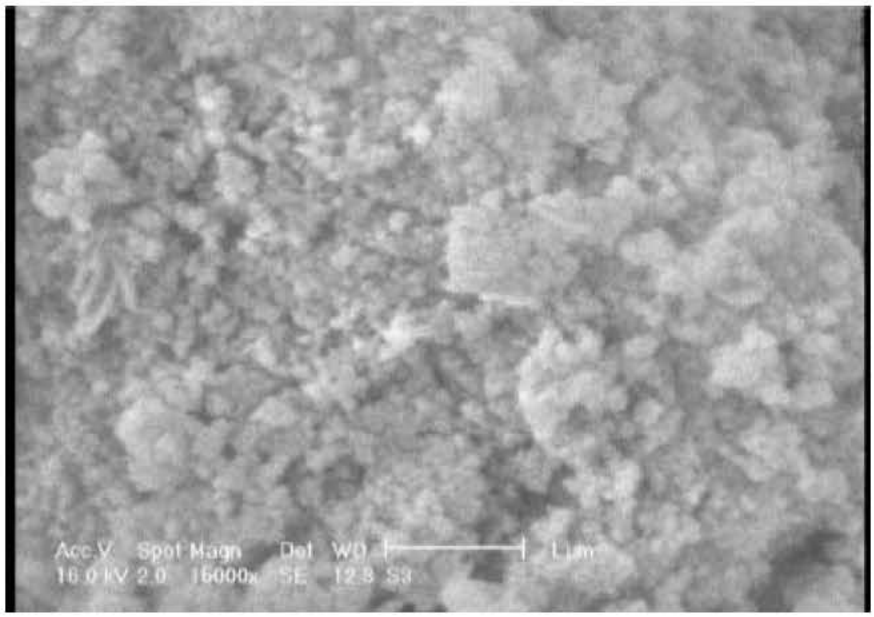

Fig. 4: SEM picture of sample BG-H9 (9 grams HPC per 1 liter)

The size and homogeneity of the particles are dependent on the concentration of surfactant. It can be concluded that when the concentration of surfactant increases, the size of particles decreases.

In conclusion, this study showed that the sol–gel low temperature process could be useful for producing nano bioactive glass-ceramic. Different sizes and shapes of sol–gel bioglass-ceramics were obtained by adding surfactant. The size of the bioactive glass particles could be controlled in the range of less than 60 nm by controlling the concentration of surfactant.

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