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Fabrication and characterization of baghdadite nanostructured scaffolds by space holder method

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ABSTRACT

Porous baghdadite scaffold has received great attention as a candidate for bone tissue engineering application due to its remarkable bioactivity, biocompatibility, and good bone formation ability. A few studies have been focused on improving the mechanical properties of baghdadite scaffolds. Recently, space holder method has been introduced as a new and viable technique to prepare bioceramic scaffolds with interconnected pores and suitable mechanical properties. In this study, for the first time, 3D baghdadite scaffolds with interconnected porosity were produced using space holder method. X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were utilized to characterize various specimens. The baghdadite scaffolds were sintered at various temperatures in the range of 1250–1350 °C for 3 h. The compressive strength and compressive modulus measured to be in the range of 0.05–0.52 MPa and 2.1–121.5 MPa, respectively. The results showed that nanostructured baghdadite scaffolds with a crystallite size of about 32 nm, 75% porosity and pores size in the range of 200–500 μm can be successfully fabricated after sintering at 1350 °C for 3 h. Simulated body fluid (SBF) was used to evaluate the apatite formation ability of the scaffolds. The results showed the formation of an apatite layer on the scaffold surface which can be considered as a bioactivity criterion.

1. Introduction

The repair of bone defects in the musculoskeletal system, such as bone, is a major clinical problem all around the world (Kariem et al., 2015; Gualandi, 2011). Only in the United States over 3 million orthopedic surgeries are performed yearly (Laurencin and Nair, 2014; Pangon et al., 2016). Over half of these procedures involve bone grafting using either an autograft or an allograft (Ramaswamy et al., 2008; Alex Jahangir et al., 2008). Autografts and allografts have been introduced as current treatment procedures for bone regeneration; however, they have some downsides such as immune rejection, the risk of infection, and tissue necrosis (Tabata, 2001; Seiler and Johnson, 2000; Hutmacher et al., 2007).

Tissue engineering is an alternative method to heal bone defects by utilizing a synthetic implant to support cell migration and establish sufficient cell-extracellular matrix (ECM) and cell-cell interactions (Kumar et al., 2007; Park et al., 2014). Utilizing bioactive ceramic scaffolds to regenerate bone tissue can speed up the healing time, prevent the rejection of implant and improve cell migration, proliferation, and vascularization; however, the main drawback of these scaffolds is their low mechanical properties (Komlev and Barinov, 2002; Roohani Esfahani et al., 2008). An ideal scaffold should have interconnected porous structure as well as pore size in the range of hundred microns to allow cell growth and delivery of nutrient (Gualandi, 2011; Gerhardt and Boccaccini, 2010). It should be noted that the pore size and mechanical properties have an inverse relationship; as a general rule, increasing the pore size decreases the mechanical properties of the scaffolds (Gualandi, 2011; Gerhardt and Boccaccini, 2010; Karageorgiou and Kaplan, 2005).

Porous bioceramics, most of all calcium-phosphate groups such as hydroxyapatite, have received much interest in tissue engineering application as a result of their excellent biocompatibility and similar chemical component to the bone. Although their low mechanical properties and biodegradability limit their usage in clinical applications (Sopyan et al., 2007; An et al., 2012).

In recent decades, development of calcium silicate-based ceramics becomes very important because of their superior biocompatibility, bioactivity, and mechanical properties in comparison to HA (De Aza et al., 2000; Sadeghzade et al., 2016). The incorporation of some elements such as Zr, Mg, Zn into the calcium silicate network has

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performed to control the biological performance and mechanical properties of the scaffolds (Wang et al., 2012; Sadeghzade et al., 2016).

Baghdadite ($Ca_3ZrSi_2O_9$) is a member of calcium silicate – zirconium group with monoclinic structure. In a recent study (Schumacher et al., 2014), the bending strength, hardness, and fracture toughness of dense baghdadite with 0.5% porosity were reported to be 98 ± 16 MPa, 7.9 ± 0.2 GPa and 1.3 ± 0.1 MPa.$m^{1/2}$, respectively, which is close to the mechanical properties of cortical bone. Furthermore, baghdadite is recognized as a bioceramic with excellent biocompatibility as well as osteoblast and osteoclast proliferation (Ramaswamy et al., 2008).

Various procedures have been developed to design biomedical scaffolds including gel-casting method (Ghomi et al., 2011), spongy method (Goudouri et al., 2014), freeze-drying (Sadeghpour et al., 2014), electro-spinning (He et al., 2014) and space holder methods (Arifvianto and Zhou, 2014; Vitale-Brovarone et al., 2008; Baino et al., 2009). Among these methods, space holder technique has received great interest due to its capability to control the size, morphology and the interconnectivity of the pores as well its appropriate mechanical properties close to the spongy bone (Arifvianto and Zhou, 2014; Sadeghzade et al., 2017).

The aim of the present research was to fabricate nanostructured baghdadite scaffolds by space holder method. Phase evaluation during synthesis procedure and the mechanism of baghdadite formation by sol-gel method were studied. The mechanical and physical properties besides the bioactivity of the prepared scaffolds were evaluated as well.

2. Materials and methods

2.1. Preparation of baghdadite powder and scaffolds

Nanostructure baghdadite powder was synthesized by sol-gel method as described in (Roohani-Esfahani et al., 2012). Briefly, to synthesize baghdadite powder, zirconium nitrate oxide ($ZrO(NO_3)_2$), calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$) and tetraethyl orthosilicate (TEOS, $(C_2H_5O)_4Si$) were selected as initial materials. TEOS, ethanol, and HNO_3 (2 M) with the molar ratio of 1:8:0.16 were mixed and was stirred for 30 min. Then $ZrO(NO_3)_2$ and $Ca(NO_3)_2.4H_2O$ were added into the solution with the molar ratio of Zr/Ca/TEOS equals to 1:3:2. Next, the solution was stirred for 5 h. Subsequently, the solution was kept at 60 °C for 1 day and dried at 100 °C for 2 days to obtain a dry gel. Finally, the dry gel was annealed at 1150 °C for 3 h.

Space holder method was utilized to produce baghdadite scaffolds. The fabrication procedure is depicted in Fig. 1. In order to prepare baghdadite scaffolds, sodium chloride was selected as a spacer agent due to its high strength rather than other organic spacers which prevent crack development during the compression process. Also, it is recognized as a non-cytotoxic material without creating the chemical reaction with the matrix (Arifvianto and Zhou, 2014; Sadeghzade et al., 2017; Ghomi et al., 2016). An appropriate amount of baghdadite nanopowder with 80 wt.% sodium chloride (NaCl, 99.9% purity, samchun) was mixed in an amalgamator. The high weight percentage of NaCl in the mixture was chosen to fabricate highly porous scaffolds. The produced powder was uniaxially pressed into pellets in a hardened steel mold at a pressure of 65 MPa by a universal testing machine (HOUNSFIELD: H50KS). Finally, the pellets were sintered at 1250 °C, 1300 °C and 1350 °C for 3 h with the heating and cooling rate of 3 °C/min to remove the spacer and strengthen the scaffolds.

2.2. Evaluations of powder and scaffold

The phase transformation was investigated by X-ray diffractometry (X' pert Philips) with CuKα radiation (λ = 0.154 nm). The XRD traces were recorded in the 2θ range of 20–70° (step size of 0.05° and time per step of 1 s). The crystallite size of different samples was measured by Scherrer equation as follows (Sadeghzade et al., 2017).

$$\beta \cos\theta = \frac{K\lambda}{D} \quad (1)$$

where D is the crystallite size, λ is the wavelength of the radiation, β is the diffraction peak width at half maximum intensity, and θ is the Bragg diffraction angle and K is the Scherrer constant.

To investigate the pore morphology and detecting the apatite on the surface of the scaffold, scanning electron microscopy (SEM, Philips XL30) at an acceleration voltage of 30 kV were used. In order to evaluate the grain size and morphology of powder, transmission electron microscopy (TEM; EM208S) were used. The compressive test with the aim of measuring the compressive strength and compressive modulus was carried out with the universal testing machine (Hounsfield, H25KS). For this purpose, samples with the height and diameter of 18 mm and 10 mm were prepared. The porosity of the scaffolds was measured based on Archimedes method (Ozgür Engin and Cüneyt Tas, 1999). In order to evaluate the apatite formation ability of the scaffolds, simulated body fluid (SBF) was used which is

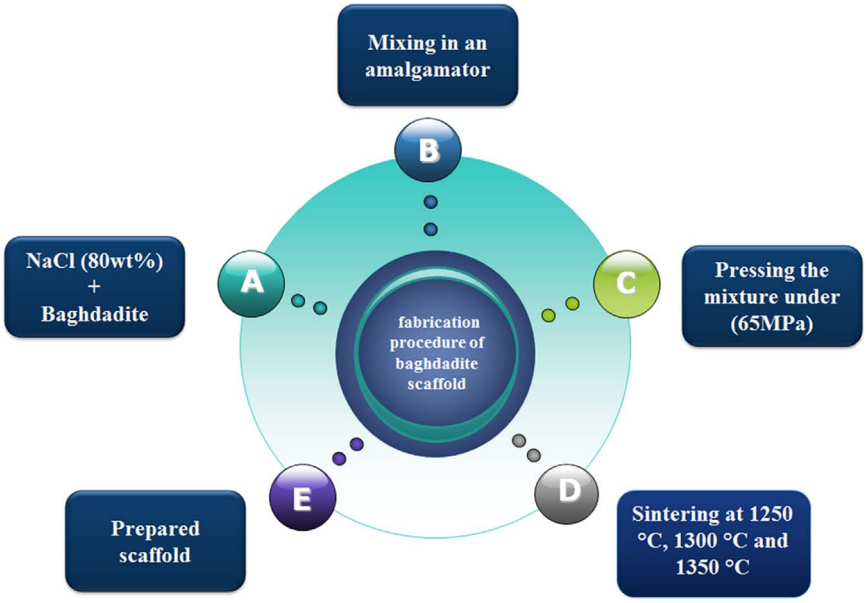

Fig.1. Fabrication procedure of baghdadite scaffold.