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Green synthesis of calcium silicate bioceramic powders

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Abstract

Calcium silicates have proven to be potential candidates for biomedical applications because of their osteogenic properties. Sol–gel methods are typically used for the preparation of calcium silicate powders. However, in the sol–gel route, an acid or base and ethanol are used to catalyze the precursors. From the perspective of green chemistry, it is better to avoid the use of organic solvents. The objective of this study was to prepare calcium silicate powders using a green synthesis route (hydrothermal method) without organic solvents. The powders were also prepared via the sol–gel process using tetraethoxysilane (TEOS) and calcium nitrate as the raw materials for the purpose of comparison. The powders were sintered at temperatures ranging from 600 to 1000 °C after the application of both methods. To understand the feasibility of using the resulting materials in medical applications for bone repair, the powders were mixed with water to form cements. The results indicated that the powder composition was not significantly affected by the different techniques but was dependent on the Ca:Si ratio of the precursors and on the sintering temperature. The different techniques produced no differences in powder morphology. In addition, the setting times of the powder-derived cements were found to be independent of the sintering temperature and synthesis technique, but it was affected by the Ca:Si ratio of the precursors. The mechanical strength of the cements was similar. These encouraging results suggest that the hydrothermal method is a potentially beneficial alternative to the sol–gel route for the production of calcium silicate powders.

Keywords: Calcium silicate; Green synthesis; Sol–gel; Hydrothermal; Bioceramics

1. Introduction

Calcium-silicate-based materials have been found to exhibit excellent bioactivity and are potential candidates for use in hard-tissue repair and regeneration [1–4]. In vitro cell culture studies have demonstrated that these bioactive materials can support the attachment, proliferation and differentiation of human bone mesenchymal stem cells [5,6], human pulp cells [7,8], and osteoblast-like cells [2]. More importantly, newly formed bone tissue can grow on calcium-silicate-based materials, along with the deposition of a bone-like apatite layer at the tissue/material interface [9,10]. Additionally, calcium-silicate-based materials exhibit some antibacterial activity to prevent bacterial growth [11]. Because material chemistry and processing together determine the highest functionality that a material can achieve, a variety of methods, including solid-state sintering, precipitation and sol–gel techniques, have been used for the preparation of bioceramic powders. In the case of calcium silicate, conventional powder fabrication technology using the melt-quenching technique requires a temperature of 1400 °C to produce ceramics; by contrast, the sol–gel approach requires relatively low temperatures of approximately 700 °C [1,12]. Sol–gel-derived ceramics exhibit better chemical and structural homogeneity and bioactivity than do ceramics obtained through conventional glass melting or ceramic powder methods such as solid-state sintering [13,14]. In a study conducted by Chang et al. [15], it has been demonstrated that a carbonate-containing hydroxyapatite layer will develop on

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the surfaces of sol–gel-prepared dicalcium silicate powders when these powders are soaked in simulated body fluid.

The sol–gel process is generally based on the polycondensation of monomeric multifunctional metal alkoxides or inorganic precursors [12]. Factors that affect the sol–gel process include the reactivity of the metal alkoxides, the pH of the reaction medium, the water:alkoxide ratio, the reaction temperature, and the natures of the solvent and the additive [16]. One typical synthesis process for calcium silicate gels is the cogelation of tetraethoxysilane (TEOS) and hydrated calcium nitrate. Because the rate of hydrolysis of TEOS is very slow in neutral solutions, this route requires the addition of an acid (e.g., acetic acid and nitric acid) or base (e.g., ammonia) catalyst during gelation [1,12]. The presence of water alone, without any catalyst, results in elastic homogeneous gel structures, which require a long drying time [12].

Green chemistry refers to the design of chemical products and processes in which the use and generation of hazardous substances are reduced or eliminated [17]. The hydrothermal method enables the synthesis of ultrafine and high-purity powders within a short processing time because of the synergistic effect of temperature and pressure. This method has been successfully applied in both organic synthesis and the preparation of inorganic materials [18]. However, the preparation of calcium silicate using the hydrothermal method has not yet been reported. Herein, we report, for the first time, a low-cost, acid-free hydrothermal synthesis route for the preparation of calcium silicate powder, using TEOS and calcium nitrate tetrahydrate as the starting materials. The objective of this study was to investigate the effects of the two synthesis technologies (sol–gel and hydrothermal) on the structure and composition of the resulting calcium silicate materials prepared using three different Ca/Si molar ratios (6:4, 5:5, and 4:6) after sintering at various temperatures. Subsequently, to further assess the feasibility of the hydrothermal method, the synthesized powders were mixed with water and the physicochemical properties of the resulting cements, including setting time and strength, were evaluated.

2. Materials and methods

2.1. Preparation of powders

Reagent-grade tetraethoxysilane ($Si(OC_2H_5)_4$; TEOS, 98.0%, Sigma-Aldrich, St. Louis, MO, USA) and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$; 98.5%, Showa, Tokyo, Japan) were used as precursors for SiO_2 and CaO, respectively. The nominal CaO:SiO_2 molar ratio was varied from 6:4 to 4:6. The general procedures for the sol−gel route, including hydrolysis and aging, were adopted from [19]. 2 M nitric acid (HNO_3) was used as the catalyst, and absolute ethanol was used as the solvent. In brief, TEOS was hydrolyzed via the sequential addition of 2 M HNO_3 and absolute ethanol, with 1 h of stirring for each. The required amount of $Ca(NO_3)_2 \cdot 4H_2O$ was added to the resulting TEOS−HNO_3−ethanol solution, and the mixed solution was stirred for an additional hour. The (HNO_3+ H_2O):TEOS:ethanol molar ratio was 10:1:10. The sol solution was hermetically sealed in a polypropylene bottle and placed in an oven for aging at 60 °C for 1 day. For hydrothermal synthesis, ready-adjusted solutions of TEOS and calcium nitrate, in water instead of ethanol and nitric acid, were placed in a Teflon vessel that was heated to a temperature 120 °C for 1 day in an oven and then allowed to cool naturally to room temperature. After the completion of the two different processes, vaporization of the solvent was performed in an oven at 120 °C. The final calcium silicate was obtained by sintering the dried gel at the desired temperature (600−1000 °C) in air for 2 h at a heating rate of 10 °C/min using a high-temperature furnace, followed by cooling to room temperature in the furnace to produce a powder. The sintered granules were ball milled for 12 h in ethanol using a centrifugal ball mill (Retsch S 100, Hann, Germany) and then dried in an oven at 60 °C. For simplicity, throughout the study, the as-sintered powders and the cements derived from those powders were designated by the same codes. For example, the specimen code "SGC4S6" represents both the sol–gel-derived (SG) powder containing 40CaO/60SiO_2 (in mol%) and the cement derived from that powder (Table 1), whereas the specimen code "HTC4S6" represents both the hydrothermally derived (HT) powder containing 40CaO/60SiO_2 (in mol%) and the cement derived from that powder.

2.2. Characterization of powders

The surfaces of the various powders were coated with gold using a JFC-1600 coater (JEOL, Tokyo, Japan), and the surface morphologies were then observed using a field-emission scanning electron microscope (SEM; JEOL JSM-7401F, Tokyo,

Table 1
Sample code, sintering temperature and Ca/Si molar ratio of calcium silicate powders prepared by the sol–gel method or the hydrothermal method (n=3).

Code	Ca/Si ratio of raw materials	Sintering temperature (°C)									
		600		700		800		900		1000	
		SG	HT	SG	HT	SG	HT	SG	HT	SG	HT
C4S6	0.67	0.63 ± 0.04	0.66 ± 0.06	0.66 ± 0.06	0.64 ± 0.06	0.63 ± 0.03	0.65 ± 0.04	0.65 ± 0.07	0.61 ± 0.05	0.65 ± 0.03	0.59 ± 0.04
C5S5	1.00	1.05 ± 0.11	0.93 ± 0.07	0.90 ± 0.03	1.00 ± 0.02	0.93 ± 0.05	0.92 ± 0.04	0.98 ± 0.12	1.12 ± 0.08	0.96 ± 0.09	1.01 ± 0.09
C6S4	1.50	1.53 ± 0.10	1.41 ± 0.11	1.42 ± 0.12	1.52 ± 0.07	1.39 ± 0.07	1.35 ± 0.02	1.44 ± 0.05	1.41 ± 0.06	1.45 ± 0.05	1.48 ± 0.04

Note: SG: sol–gel method; HT: hydrothermal method.