Synthesis and Characterization of Novel Nanodiopsidebioceramic Powder

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Abstract

Diopside has been successfully prepared by a modified sol-gel method.Optimization in calcination temperature and mechanical ball milling resulted in a pure and nano-sized powder which characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and fourier transform infrared Spectroscopy (FT–IR). We hypothesized that nano-sized diopside would mimic more efficiently the nanocrystal structure and function of natural bone apatite, owing to the higher surface area, compare to conventional micron-size diopside. Accordingly, we used the unique advantage of nanotechnology to improve novel nanodiopside particles as a potential candidate for bone tissue regeneration whether as a peri-implant filling powder or in combination with other biomaterials as a composite scaffold.

1. Introduction

Nanotechnology has a great potential to improve ultimate biomaterials used for tissue engineering. Engineering systems for controlled release of biological nanomolecules and supplementing scaffolds with inorganic nanoparticles improve tissue function by means of mimicking the natural external cell matrix (ECM).Many attempts in the field of engineering novel nanobiomaterials played a key role in the recapitulation of the basic building blocks of native microenvironment of the cells for replacing tissue deficiencies like bone losses from trauma or diseases [1]. Upon this, the approach of incorporating inorganic nanoparticle into the matrix will progress rapidly. Although

various inorganic nanomaterials have been used to replace damaged bones [1-11] but silicate biomaterials such as bioglass, $CaSiO_3$ and Ca–Si–M (M = Mg, Zn, Ti, Zr) ceramics have a significant characteristic of the ability to release Si ions at a concentration that stimulates osteoblast growth and differentiation suggesting their application for bone tissue regeneration [12]. The superiority of these ceramics in bone tissue regeneration compare to hydroxyapatite and other ceramic scaffolds have been reported and among them diopside with the chemical formula of $CaMgSi_2O_6$ both in powder or bulk form possesses slower degradation rate and efficiently has the ability of invitro apatite formation and invivo bone regeneration [3]. Diopside powders and dense ceramics have been shown to be bioactive material for bone regenerations in biomaterial science. Wu and Chung proved the quite better cell growth on diopside disks compare to the other members of $CaOSiO_2$-MgO systems like bredigite and akermanite as a result of the reduction in their degradation rates [3]. Moreover, this ceramic is higher in mechanical properties when it is synthesized in a dense bulk format. Excellent mechanical stability, high bioactivity properties and appropriate cell biocompatibility features due to slow degradation rate made the diopside ceramic a hot point of concern among biomaterialists. In addition, various powder preparation methods have been reported such as solid state reaction, sol-gel, coprecipitation and spray pyrolysis technique [2-12]. Among them sol-gel technique was chosen to obtain pure and homogenous diopside with no extraneous phase. However, to the best of our knowledge, in none of the previous studies that focused on diopside powder or bulk scaffolds preparation and characterization, interests has been taken to the preparation of this exceptionally advantageous bioceramic in nano-size powder format.

Keeping the above points in view, this study was aimed to report the chemical synthesis and characterization of the sol-gel prepared bone-like powder of diopside in a nanostructure type. When we consider replacing bone deficiencies with a synthetic material, it is necessary to mimic natural bone nanostructure as much as possible. In this trend, we have focused on developing a substitute for biological apatite in a submicron level considering the advantage of high surface area owing to the nanostructure dimensions.

2. Experimental

2.1. Materials and characterization

Calcium nitrate, magnesium nitrate, TEOS and all other solvent and chemicals were analytical grade from Sigma Chemical (St. Louis, MO, USA). A zirconia mechanical ball mill (Daehan science, Seoul, Korea) has been used to ensure the smallest particle sizes of the ceramic powder.The morphology of diopside nanoparticles was examined by Scanning Electron Microscopy (SEM, JEOL JSM-6300, Tokyo, Japan). The nanopowders were mounted onto sample studs and coated with gold using a sputter-coater (Eiko IB3, Tokyo, Japan) for 3min. The microscope was operated at 15 kV to visualize the sample.

The phase composition and structure of prepared samples were examined by X-ray powder diffraction (XRD). A Philips X'PERT-MPD X-ray diffractometer (XRD) with Cu Kα radiation at a scan rate of 0.02◦/min was used for the crystallographic structural analysis of the sample.

Transmission electron microscopy (TEM, JEOL JSM-7600F field emission transmission electron microscope) was used to determine the particle size of sol–gel prepared diopside powders. Sample preparation has been done by obtaining a suspension from ultrasonification of the powder in ethanol on a foil surface followed by dropping on a cupper grid and finally dried to capture the images by means of TEM.

A JASCO FT/IR-680 PLUS spectrometer was used to record IR spectra using KBr pellets. FT-IR spectra of the catalysts were recorded by FT-IR spectrophotometer in the range of 400–2000 cm^{-1} with a resolution of 4 cm^{-1} by mixing the sample with KBr.

2.2. Preparation of diopsidenanopowder

The diopside ceramic was prepared via a modified sol-gel method. Briefly we dissolved a same molar ratio of $Ca(NO_3)_2.4H_2O$ and $MgCl_2.6H_2O$ in an absolute ethanol and stirred vigorously for 30 minutes in 80 ℃ to dissolve these precursors in the solvent. $Si(OC_2H_5)_4$ (TEOS) was added to the homogenous solution and slowly stirred to transform to a wet gel. Drying in an oven at 100 ℃ for 24 hours resulted in a dried powder which was grounded in a hand-mortar, then calcined at 700 ℃ for 2 h and 1100 ℃ for further 24 hours. Finally it was ball-milled in a zirconia mechanical ball mill for 8 hours to supply diopsidenanopowder.

3. Results and discussion

Preparing micron size diopside by means of sol-gel method has been previously reported [12] but here some modifications in the post-treatments of the as-prepared ceramic including thermal

treatments and mechanical manipulations resulted in a pure diopsidenanopowder with particle sizes in the range of 35-65 nm.The diopside grain size and surface morphology of the particles are shown in Figure.1, indicating that particles agglomerated as a result of high surface energy. However, it is obvious that the dimensions of agglomerated grains are in nano range.
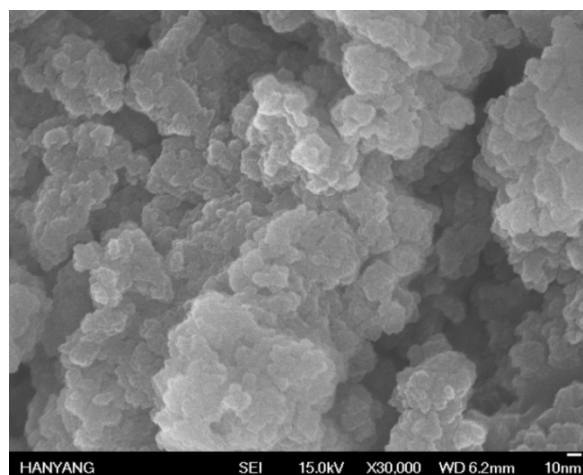
Fig.1.SEM micrograph of diopsidenanopowders.

Figs. 2 and 3 show the XRD patterns of the diopsidenanopowders prepared via the sol-gel method and calcined at different temperatures. Calcination at 700 °C resulted in no characteristic peak (Fig.2). Critical calcination temperature of 1100 °C was obviously ideal to obtain pure diopside with no impurity of other ceramics. It yielded strong diopside peaks at about 220°, 221°, 310°, 311°, 131°, which indicates that the dominant resultant of the process is diopside (fig3). However, in the sample calcined at temperatures below 1100° C, akermanite, and in higher tempratures, bredigite ($Ca_2MgSi_2O_7$) was detectable.

Furthermore, it is possible to estimate the crystallite size (x_s) in a direction perpendicular to the crystallographic plane of XRD reflection [13].

Sharper and isolated diffraction peaks such as $2\theta=56.675$ were chosen for calculation of the crystallite size. Based on the Debye-Scherrer's formula ($X_s=\frac{0.9\lambda}{FWHMcos\theta}$), FWHM is the full width at half maximum for the chosen diffraction peaks in rad (in this case FWHM is equal to 0.003663) and λ is the wavelength of x-ray beam for Cu Kα radiation ($\lambda=1/542$ nm). Accordingly, the average crystallite size of 38.153 was calculated. None of the other chosen peaks for estimation of crystallite size exceeded the result of 45 nm.

Fig. 2. Phase composition of diopsidepowders calcined at different temperatures of 700 °C (a) and 1100 °C(b)**.**

Fig. 3 presents the TEM micrograph of the 1100 °C heat-treated diopside and taken images enables the detailed observation of the morphological properties of particles. It shows the spherical border of a non-agglomerated monodispersive particle and particle size of 65 nm.

Fig. 3. TEM micrograph of diopside nanoparticles

In the FT-IR spectra of the diopside bands (fig. 4) in the 400–2000 cm^{-1} spectral range in the region 700 cm^{-1} can be attributed to the bending vibrations, and bands in the region 850–1100 cm^{-1} which are attributed to the stretching vibrations of the silicate structure. They ascribed to the Si–O symmetric stretching of bridging & non-bridging oxygen atoms, Si–O–Si symmetric stretching, and Si–O–Si asymmetric stretching. Our results are in agreement with previous studies [14].

Fig. 4. FT-IR spectra of the diopside nanoparticles

4. Conclusion

Pure diopside powders were successfully obtained via a simple sol-gel method followed

by calcination at 1100 °C. Mechanical grinding in a ceramic ball mill for 8 hours resulted in diopside nanoparticles in the range of about 35-65 nm. Conventional micron-size diopside had been previously investigated by many researchers but it is obviously different from bone mineral in aspect of mimicking the mineral resorption process. Bone crystals of hydroxyapatite are in nano-size dimensions and possess very large surface area. In contrast micron-size particles with lower surface area, lack the potency of homogeneous absorption by osteoclasts and miss the unique advantage of nanotechnology for bioactivity and resorbability. Our study suggests that nanodiopside might be a potential candidate by itself as a nanobioceramic filling powder or in combination with other biomaterials as a composite scaffold in bone tissue regeneration.

Acknowledgment

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