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Characterization and synthesis of hardystonite (HT) as a novel nanobioceramic powder

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ABSTRACT

Objective(s): Hardystonite (HT) has been successfully prepared by a modified sol-gel method. We hypothesized that nano-sized (HT) would mimic more efficiently the nanocrystal structure and function of natural bone apatite, owing to the higher surface area, compare to conventional micron-size (HT).

Materials and Methods: The hardystonite nanopowder was prepared via a modified sol-gel method.Optimization in calcination temperature and mechanicalball milling resulted in a pure and nano-sized powder which was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and fourier transform infrared spectroscopy (FTIR).

Results: Pure (HT) powders were successfully obtained via a simple sol-gel method followed by calcination at1150 °C. Mechanical grinding in a ceramic ball mill for 6 hours resulted in (HT) nanoparticles in the range of about 32-55nm.

Conclusion: Our study suggested that nanohardystonite (NHT) 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.

Keywords: *Hardystonite (HT), Nanobioceramic powder, X-Ray diffraction, TEM, SEM, FTIR*

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

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damaged bones [1-13] but silicate biomaterials such as bioglass, CaSiO3 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 (HT) with the chemical formula of ($Ca_2ZnSi_2O_7$) both in powder or bulk form possesses slower degradation rate and efficiently has the ability of invitro apatite formation and invivo bone regeneration [3]. Hardystonite (HT) 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 disks compare to the other members of CaOSiO2-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 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 with no extraneous phase. However, to the best of our knowledge, in none of the previous studies that focused on 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 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.

MATERIALS AND METHODS

Calcium nitrate, magnesium nitrate, TEOS and all other solvent and chemicals were analytical grade from Sigma Chemical (Sc. Litch, MO, USA). A zirconia mechanical ball mill (Saha science, Ben, Germany) has been used to ensure the smallest particle sizes of the ceramic powder.

The morphology of nanoparticles was examined by Scanning Electron Microscopy (SEM, Hitachi JSM-6500, 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'PERTMPD X-ray diffractometer (XRD) with Cu Kαradiation 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 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 ZAIES FT-IR-560 + 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 200–1800 cmH1 with a resolution of 4 cmH1 by mixing the sample with KBr.

Preparation of hardystonite nanopowder

The ceramic was prepared via a modified sol-gel method. Briefly we dissolved a same molar ratio of Ca(NO3)2.4H2O and MgCl2.6H2O in an absolute ethanol and stirred vigorously for 20 minutes in 90 ℃ to dissolve these precursors in the solvent. Si(OC2H5)4 (TEOS) was added to the homogenous solution and slowly stirred to transform to a wet gel. Drying in an oven at 110 ℃ for 24 hours resulted in a dried powder which was grounded in a hand-mortar, then calcined at 750 ℃ for 2 h and 1150 ℃ for further 24 hours. Finally it was ball-milled in a zirconia mechanical ball mill for 6 hours to supply hardystonitenano powder.

RESULTS AND DISCUSSION

Preparing micron size by means of sol-gel method has been previously reported [10-11] but here some modifications in the post-treatments of the as-prepared ceramic including thermal treatments and mechanical manipulations resulted in a pure hardystoni-tenanopowder with particle sizes in the range of 32-55 nm. The grain size and surface morphology of the particles were show in Fig.1, indicating that particles agglomerated as a result of high surface energy. However, it was obvious that the dimensions of agglomerated grains were in nano range.

Fig. 2 show the XRD patterns of the hardystonite nanopowders prepared via the sol-gel method and calcined at different temperatures. Calcination at 750 °C resulted in no characteristic peak .

Critical calcination temperature of 1150 °C was obviously ideal to obtain pure with no impurity of other ceramics. It yielded strong peaks at about 221°, 220°, 311°, 310°, 131°, which indicates that the dominant resultant of the process is (Fig. 3). However, in the sample calcined at temperatures below 1150 °C, akermanite, and in higher tempratures, bredigite Ca2MgSi2O7) was detectable. Furthermore, it is possible to estimate the crystallite size (xs) in a direction perpendicular to the crystallographic plane of XRD reflection [13-14].
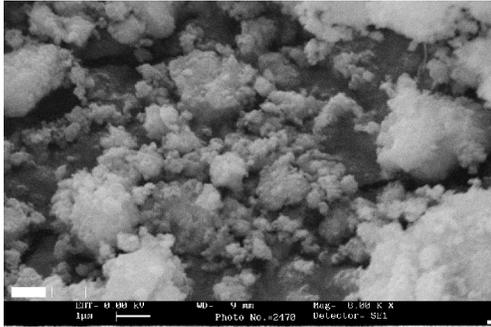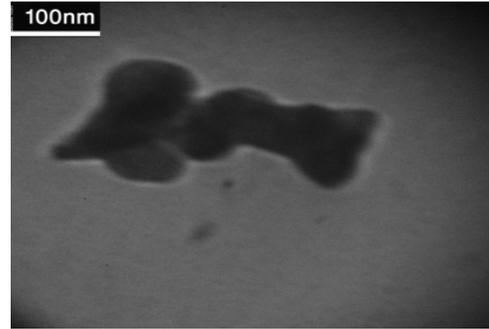
Fig. 1. SEM micrograph of hardystonitenanopowders

Fig. 3. TEM micrograph of hardystonite nanoparticles

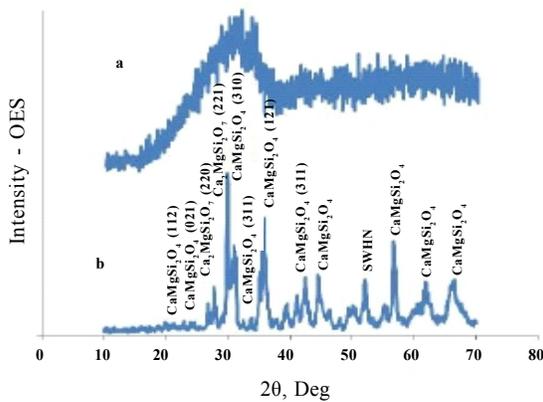
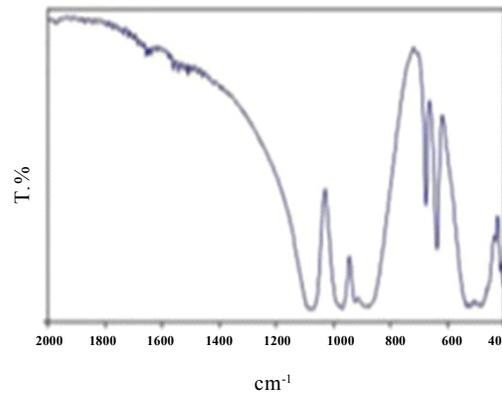Fig. 2. Pattern of hardystonitepowders calcined at different temperatures of 750 °C (A) and 1150 °C (B)

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

Sharper and isolated diffraction peaks such as $2\theta = 56.675$ were chosen for calculation of the crystallite size. Based on the Modify Sherrer formula ($L = K\lambda/\beta.\cos\theta$), FWHM is the full width at half maximum for the chosen diffraction peaks in rad (in this case FWHM is equal to 0.003662) and λ is the wavelength of x-ray beam for Cu Kαradiation ($\lambda = 1/542$ nm).

Accordingly, the average crystallite size of 39.153 was calculated. None of the other chosen peaks for estimation of crystallite size exceeded the result of 40 nm. In fig. 3, TEM micrograph of the 1150 °C heat-treated samples was shown the spherical border of a nonagglomerated Monodispersive particles in the range of 32 to 55 nm.

In the FT-IR spectra of the bands (fig. 4) in the 400–2000 cm^{-1} spectral range in the region 750 cm^{-1} could be attributed to the bending vibrations, and bands in the region 800– 1050 cm^{-1} which was attributed to the stretching vibrations of the silicate structure.

CONCLUSION

Pure powders were successfully obtained via a simple sol-gel method followed by calcination at 1150 °C. Mechanical grinding in a ceramic ball mill for 6 hours resulted in nanoparticles in the range of about 32- 55 nm. Conventional micron-size 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 suggested that nanohardystonite (NHT) 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.

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