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RESEARCH ARTICLE

Survey and Evaluation of Merwinite (MW) as a New Nanobioceramic Powder

Hassan Gheisari**, Ebrahim Karamian, Ali Soheily

Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University,Najafabad, Iran

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ABSTRACT

In this study, Merwinite (MW), has been successfully prepared by a modified sol-gel method. Optimization in calcination temperature and mechanical milling resulted in a pure and nano-sized powder which characterized by means of (XRD), (SEM), (TEM) and (FT–IR). We hypothesized that nano-sized MW would mimic more efficiently the nanocrystal structure and function of natural bone apatite, owing to the higher surface area, compared to conventional micron-size MW. Mechanical grinding in a ceramic ball mill for 6 hours resulted in (MW) nanoparticles in the range of about 33- 55 nm. Conventional micron-size MW 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 natural hydroxyapatite (NHA) 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. Hence, we used the unique advantage of nano- biotechnology to improve novel nano merwinite (NMW) particles as a good candidate for tissue regeneration whether as a peri-implant filling powder or in combination with other biomaterials as a composite scaffold.

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INTRODUCTION

The science of 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. Moreover various inorganic nanomaterials have been used to replace damaged bones [2-5] 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 [6-8]. The superiority of these ceramics in bone tissue regeneration compare to hydroxyapatite and other ceramic scaffolds have been reported and among them MW with the chemical formula of $Ca3Mg(SiO4)2$ both in powder or bulk form possesses slower degradation rate and efficiently has the ability of invitro apatite formation and invivo bone regeneration [9-11]. MW powders and dense ceramics have been shown to be bioactive material for bone regenerations in biomaterial science. Wu

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* Corresponding Author Email: *Hassan.gh.d@gmail.com*

and Chung proved the quite better cell growth on MW disks compare to the emother members of CaOSiO2-MgO systems like hardystonite and akermanite as a result of the reduction in their degradation rates [12]. In addition to, 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 theMW ceramic a hot point of concern among biomaterialists. In addition, various powder preparation methods have been reported such as a solid state reaction, sol-gel, coprecipitation and spray pyrolysis technique [13-16]. Among them sol-gel technique was chosen to obtain pure and homogenous MW with no extraneous phase. However, to the best of our knowledge, in none of the previous studies that focused on MW powder or bulk scaffolds preparation , investigation 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 (MW) 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 research, we focused on developing a substitute for biological apatite in a submicron level considering the advantage of high surface area owing to the nanostructure dimensions.

EXPERIMENTAL

Materials and Methods

Magnesium nitrate, Calcium nitrate, TEOS and all other solvent and chemicals were analytical grade from Sigma Chemical (SIMONS, MO, USA). A zirconia mechanical ball milling (Taha science, Ben, Germany) has been used to ensure the smallest particle sizes of the ceramic powder. The morphology of (MW) nanoparticles was examined by Scanning Electron Microscopy (SEM, Philipps wed-5911, Tokyo, Japan). The nanopowders were mounted onto sample studs and coated with gold using a sputter-coater (Eiko IF3, Tokyo, Japan) for 4min. 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 0.002°/min was used for the crystallographic structural analysis of the sample.

Transmission electron microscopy (TEM, JEOL JSM-7400F field emission, transmission electron microscope) was used to determine the particle size of sol–gel prepared (MW) powders. Sample preparation has been done by obtaining a suspension from ultra sonification 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 HITACHI FTIR-655 + spectrometer was used to record IR spectra using KBr Pellets. FT-IR spectra of the catalysts were recorded by FTIR spectrophotometer in the range of 200–2000 cm^{-1} with a resolution of 6 cm^{-1} by mixing the sample with KBr.

Preparation of merwinite nano-powder

The MW 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 25 minutes in 85 °C to dissolve these precursors in the solvent. Si(OC2H5)4 (TEOS) was added to the homogenoussolution and slowly stirred to transform to a wet gel. Drying in an oven at 125 °C for 12 hours resulted in a dried powder which was grounded in a hand-mortar, then calcined at 700 °C for 3 h and 1150 °C for further 26 hours. Finally it was ball-milled in a zirconia mechanical ball mill for 7 hours to supply merwinite nano-powder.

RESULTS AND DISCUSSION

Preparing micron size MW 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 Merwenite MW nano-powder with particle sizes in the range of 33-55 nm. The MW grain size and surface morphology of the particles are shown in Fig. 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.

Figs. 2 show the XRD patterns of the merwinite-nano-powder, 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 1000 °C was

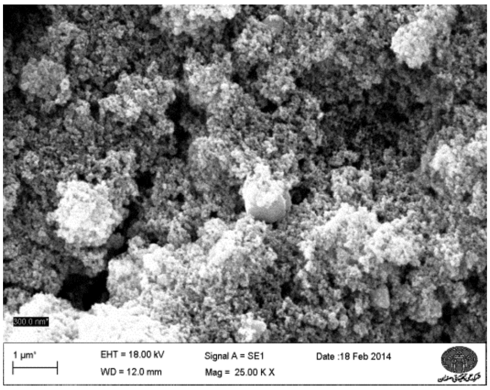

Fig.1. SEM micrograph of merwinite nano-powder

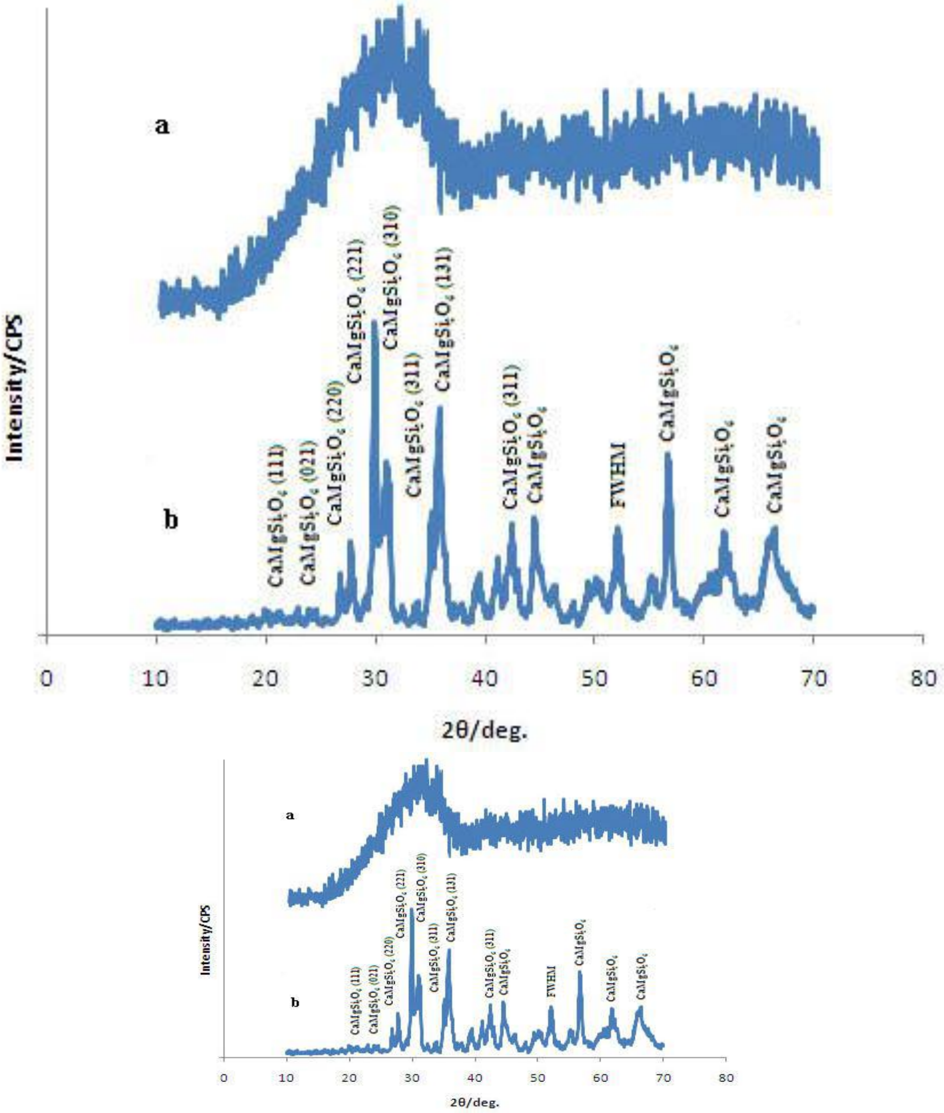

Fig.2. Pattern of merwinite powders calcined at different temperatures of 700 ◦C (A) and 1150 ◦C (B)

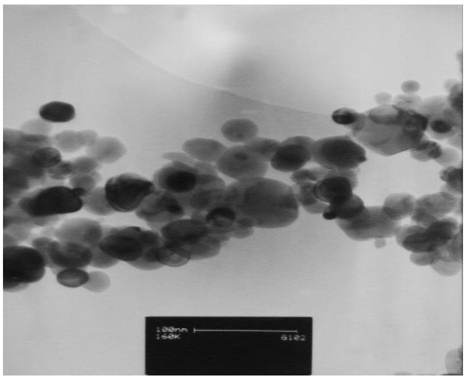

Fig. 3. TEM micrograph of merwinite MW nanoparticles

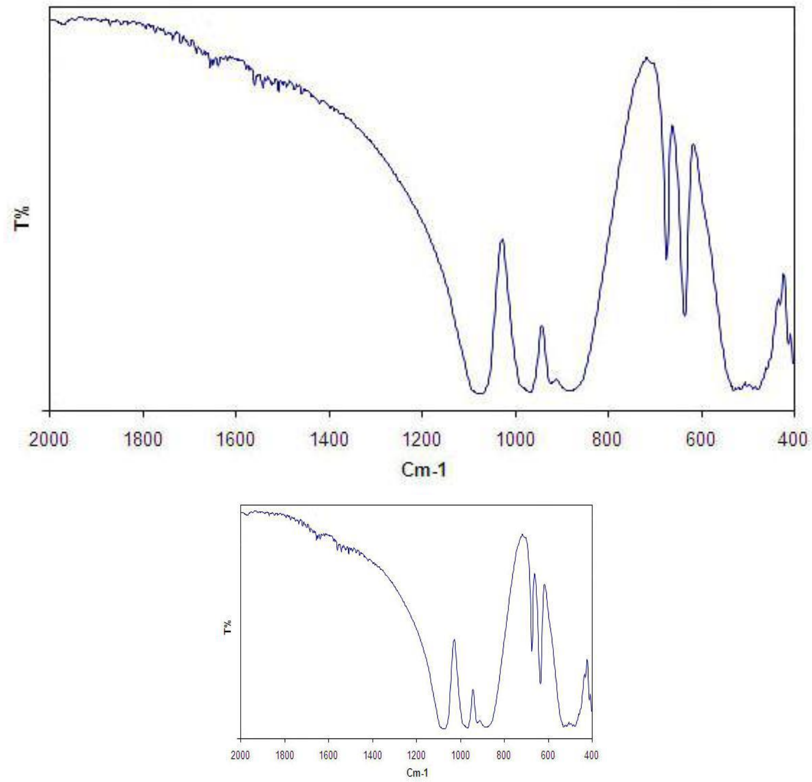

Fig.4. FTIR spectra of the (MW) nanoparticles

obviously ideal to obtain pure MW with no impurity of other ceramics. It yielded strong (MW) peaks at about 121°, 120°, 312°, 311°, 131°, which indicates that the dominant resultant of the process is MW, [12] (Fig. 3.). However, in the sample calcined at temperatures below 1000° C, akermanite, and in higher temperatures, hardystonite 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]. Sharper and isolated diffraction peaks such as 2θ=56.655 were chosen for the 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 0.002663) and λ is the wavelength of x-ray beam for Cu Kαradiation (λ=1/542 nm). Accordingly, the average crystallite size of 39.173 was calculated. None of the other chosen peaks for estimation of crystallite size exceeded the result of 38 nm.

Fig. 3 presents the transmission electron microscopy (TEM) micrograph of the 1150 °C heat-treated MW and taken images enables the detailed observation of the morphological properties of particles. It shows the spherical border of a non-agglomerated mono dispersive particle and particle size of 55 nm.

In the FT-IR spectra of the MW bands (Fig. 4) in the 400–2000 cm^{-1} spectral range in the region 750 cm^{-1} can be attributed to the bending vibrations, and bands in the region 700– 1000 cm^{-1} which are attributed to the stretching vibrations of the silicate structure. They ascribed to the Si–O symmetric stretching of merwinite & non-bridging oxygen atoms, Si–O–Si symmetric stretching, and Si–O–Si asymmetric stretching. Our results are in agreement with previous studies [16].

CONCLUSION

Pure (MW) 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 (MW) nanoparticles in the range of about 33- 55 nm. Conventional micron-size (MW) had been previously investigated by many researchers but it is obviously different from bone mineral in the aspect of mimicking the mineral resorption process. Bone crystals of natural hydroxyapatite (NHA) 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 nanomerwinite (NMW) might be a potential candidate by itself as a nanobioceramic filling powder or in combination with other biomaterials as a composite scaffold in bone regeneration.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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