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Mg-doped hydroxyapatite nanoplates for biomedical applications: A surfactant assisted microwave synthesis and spectroscopic investigations

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ABSTRACT

Nanoplates of Mg doped hydroxyapatite (Mg-HAp) were derived successfully and rapidly via microwave irradiation technique. Hydroxyapatite (HAp) is the hard tissues and main inorganic component in mammals. Different nanostructures of HAp exist in different parts of human bone but nanorods are very common due to its intrinsic nature to grow in rode-like structure under physiological as well as under applied ambient conditions in laboratory. On the addition of Mg at very low level (0.06 mol%) in pure HAp results the formation of 2-D plate-like nanostructures rather than rod-like which is the matter of interest. In this attempt our efforts have been focused on the study of effect of Mg incorporation on structural and spectroscopic properties of HAp prepared via microwave irradiation technique. This technique is preferred due to several advantages *viz.* very fast as well as homogeneous heating, time/energy saving and eco-friendliness. The calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) as a source of calcium, magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) as a source of magnesium, disodium hydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$) as a source of phosphorous and sodium ethylene diamine tetra acetate (NaEDTA) as a surfactant were used as starting reagents. Sodium hydroxide (NaOH) pellets were employed to adjust the pH value of final solution. The solution of fixed pH value was kept into the microwave oven generating waves of frequency 2.45 GHz (water absorption frequency) and power 750 W for 8 min. The precipitate thus obtained was washed, centrifuged and then dried at 100 °C for 2 h. Dried powder was then calcined at 700 °C for 2 h. The bright white powder thus obtained was characterized structurally using X-ray diffraction and SEM techniques and spectroscopically by FT-IR and Raman techniques. Structural and spectroscopic analysis revealed the formation of Mg doped HAp [Mg-HAp: $(Ca_{4.94}Mg_{0.06})(PO_4)_3OH$], nanoplates having average crystallite size of 26 nm as estimated by Scherrer's formula.

1. Introduction

Hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$ or $Ca_5(PO_4)_3OH$) is the main constituent mineral of bone and the teeth in mammals. It has attracted attention of materials scientists from past several decades, due to its crystallographic and chemical similarity with various calcified tissues of vertebrates [1,2]. HAp shows excellent biocompatibility with hard tissues like bone and teeth as well as with soft tissues like skin and muscles without showing any cytoxic effect. It promotes osseointegration and provides a surface for anchorage-dependent osteoblast to deposit calcium containing minerals, when used in orthopedic and dental implantations hence it lies in category of bioactive materials. It is also labeled as osteoconductive due to its ability to bond strongly with natural bone tissues [3]. Along with these merits, pure synthetic HAp has a demerit of incapability for load bearing due to its poor mechanical strength especially in wet environments [4]. In order to enhance the mechanical strength of pure HAp, numerous ideas have been attempted. One of the successful ideas is to use HAp powder as coating material on implants. HAp is deposited on Ti alloys by different techniques. Ti and its alloys have been found suitable for this purpose. Recently, Zhuravleva et al. [5] have reported the electrochemical deposition of HAp on porous low modulus Ti—Nb alloy

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for biomedical applications while, Durdu et al. [6] have reported the deposition of HAp on Ti—Al alloy via plasma electrolyte oxidation for the same purpose.

Incorporation of dopant creates disorders and defects in HAp crystal lattice [7,8]. André et al. [7] reported Eu doped HAp nanorods and influence of Eu^{3+} in the HA structure in a short-range order was performed by FT-Raman analyses as a complementary study for XRD data. It was concluded that Eu^{3+} substitution in HAp lattice is site-selective and incorporation of Eu^{3+} prefers Ca(II) over Ca(I) site. Mene et al. [8] prepared Fe doped HAp thick films modified via swift heavy ion irradiation has been developed for CO and CO2 gas sensing applications. Enamel, dentine and bone contain the trace amount of K, Na, Mg, F, K, Zn and CO_3 ions, which are known to play role in performance of apatite [3,9]. Mg associated with biological apatite is undoubtedly found to be one of the most important bivalent ions. Webster et al. [10] reported that 2 mol% doping of Mg^{2+} in HAp enhance the osteoblast adhesion strength as compared to pure HAp. However, doping of 20 wt% Mg^{2+} in apatite reduces the conductivity of an apatite with osteoblast cell which shows that too much substitution of dopant exceeds the doping benefits [3,11]. Landi et al. [12] reported the low concentration Mg and $MgCO_3$ play important roles in early stages of osteogenesis simulating osteoblast proliferation. Ponderosity of association of Mg^{2+} in pure HAp motivated us to synthesize Mg doped HAp powders at very low doping level (0.06 mol%) for further studies, its functionalization and biological response including mechanical strength. Mg-HAp material may have better compatibility than pure HAp, when deposited on Ti—Al alloys and others for implantation purpose. The bioactivity and biocompatibility of Mg-HAp on implantation purposes and in some other biological applications is expected to be enhanced significantly due to the presence of Mg since Mg is found in natural enamel, dentine and bone in traces. Incorporation of Mg in to pure calcium HAp makes it closer to the natural bone. Other important aspect of present work is changed surface morphology, means change in nanostructure grown in Mg-HAp. The natural bone exhibits the natural nanoparticles of hydroxyapatite crystals generally with rod or needle-like shapes, forming the composite with polymeric matrix of collagen type I. The range of particle size of natural HAp nanostructures formed in normal physiological conditions in human is 10–80 nm. In some parts of the human bone nanostructures of HAp are found in plate like shape [13]. Therefore, it will be interesting to grow the HAp nanoparticles as plate-like and additionally, to study the effect of Mg incorporation on structural (morphological) and spectroscopic properties of HAp prepared via microwave irradiation. The HAp nanoplates at very low doping level of Mg are expected to have excellent biocompatibility with hard and soft tissues comparable to pure HAp. The trace amount of Mg is present in the natural hard tissues grown as plate or rod like nanostructures in completely physiological conditions. Therefore, the artificial bone material: Mg-HAp as synthesized here is expected to be compatible and favorable with the natural bone tissues for regeneration and ingrowths in bone healing. It may also be more suitable material (than pure HAp) for coating on Ti–Al alloys as substitute of bone. Several techniques *viz.* are sol–gel [14,15], hydrothermal [16,17], combustion synthesis [18], emulsion technique [19], mechanochemical [20], radio frequency induction plasma [21], precipitation method [2], microwave irradiation technique [22–24] have been developed to synthesize HAp. We have used microwave irradiation technique in the synthesis of Mg-HAp nanoparticles due to its remarkable benefits. This technique has two noticeable advantages; one is very fast and homogeneous heating results the least processing time means energy saving as compared to other techniques and the other is that it is ecofriendly. Apart from these advantages, this technique is unique due to its almost 100% efficiency, which means that almost 100% of electromagnetic energy is converted into heat. The technique may also be employed to form ultrafine nanostructured crystalline material of high purity. Microwave oven generating microwaves of certain energy corresponding to frequency 2.45 GHz and power 750 W was employed here for eight minutes only, to get HAp nanoparticles. Therefore we can say that microwave technique has been found extremely fruitfully exploitable, time saving, energy saving and environment friendly technique in present investigations. Microwave setup used in present synthesis is shown in Fig. 1.

Interaction of microwaves with the reactants is reported recently by Mishra et al. [25]. It is speculated that during the interaction of microwaves with dielectric material, the dipoles of the dielectric are just unable to follow the quick change of high frequency electric field of microwaves. The permanent dipoles existing in the dielectric are very sensitive to the external electric field. These dipoles try to reorient themselves with external field. But a phase difference is created between applied field and dipoles due to viscosity which causes the energy to be lost in random collisions leading to dielectric heating. This phenomenon occurs in dielectrics while, the dipolar polarization is the phenomenon responsible for microwave heating and is observed only in polar solvent systems as in case of present synthesis. At low frequencies of applied electromagnetic waves, dipoles get sufficient time to align themselves with the external field and only a small energy is lost leading to little heating. In case of high frequency of applied electromagnetic field, dipoles do not have sufficient time to respond to the high frequency applied field. Therefore they do not able rotate themselves according to field resulting no motions in the molecule means no transfer of energy, hence no heating effect. Therefore, the frequency of the applied electromagnetic field must be suitable for the response time of the dipoles. Microwave region (lower as well as higher frequencies) of entire electromagnetic span fulfils this condition of suitable response time so it gives dielectric heating on interaction with dielectrics while, most efficient frequency is 2.45 GHz. This frequency of microwaves is

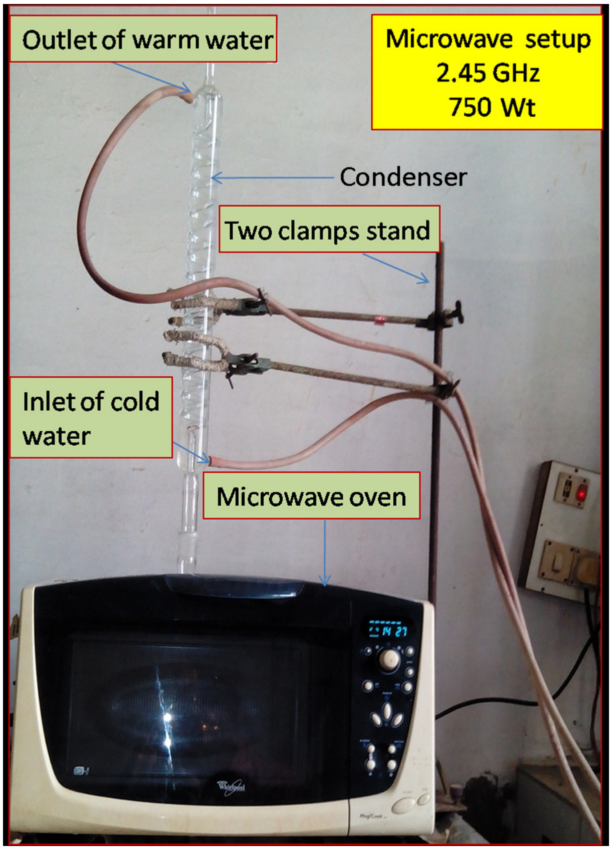

Fig. 1. Microwave setup employed in present synthesis.