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Rapid synthesis and characterization of silicon substituted nano hydroxyapatite using microwave irradiation

Sanosh Kunjalukkal Padmanabhan*, Ehsan Ul Haq, Antonio Licciulli

Department of Engineering for Innovation, University of Salento, Lecce 73100, Italy

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A B S T R A C T

Nano sized hydroxyapatites with silicon substitution of three different silicon concentrations were successfully prepared first time by a rapid microwave assisted synthesis method, with a time saving and energy efficient technique. The effects of the Si substitution on crystallite size, particle size and morphology of the powders were investigated. The crystalline phase, microstructure, chemical composition, and morphology and particle size of hydroxyapatite and silicon substituted hydroxyapatites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and dynamic light scattering. The crystallite size and particle size decreases with increase in silicon content and particle morphology spheroidal for pure hydroxyapatite changes to elongated ellipsoidal crystals while silicon substitution increases. Fourier Transform Infrared Spectroscopy analysis reveals, the silicon incorporation to hydroxyapatite lattice occurs via substitution of silicate groups for phosphate groups. Substitution of phosphate group by silicate in the apatite structure results in a small increase in the lattice parameters in both *a*-axis and *c*-axis of the unit cell.

1. Introduction

Hydroxyapatite, [$Ca_{10}(PO_4)_6(OH)_2$, HA], has achieved significant interest as a biomedical material for bone repair, such as bone-filling materials, biocompatible coatings for metal implant and inorganic/organic composite tissue engineering scaffolds. However, a disadvantage of using pure HA implants is that its reactivity with existing bone is low [1] and therefore it integrates relatively slowly with bone [2]. These properties could have implications for the time required for patient rehabilitation [3]. The development of enhanced synthetic materials for use in orthopedic implants to replace lost or damaged human bone is a continual goal of biomaterials research.

Silicon (Si) is an essential trace element in bones and studies have indicated the importance of silicon in increase the rate of biomineralization and bone regeneration by promoting extracellular matrix secretion of chondrocytes [4]. On the other hand, it has been reported that Si deficiency could lead to various bone diseases revealed by animal experiments [5–7]. These findings lead to the use of Si-substituted hydroxyapatite (Si-HA) to improve osseointegration and thus promote early bone healing. Silicon substituted hydroxyapatite is an interesting candidate for biomedical application due to its enhanced bioactivity compared with pure hydroxyapatite. Synthetic Si-HA has shown enhanced in vitro apatite formation in simulated body fluid (SBF), increased in vitro cell proliferation and creation of focal points of adhesion, as well as in vivo bone ingrowth and remodeling [3,8–12]. For these reasons, there has been interest in synthesizing silicon-substituted hydroxyapatite (Si-HA). Several methods for the synthesis have been reported including sol–gel [13], hydrothermal [14], solid-state reaction [15], chemical precipitation, and crystallization [8]. However, these processes need long processing time and the hydroxyapatite powders obtained thereof include other crystalline phases depending on the substitution degree of silicon [11].

Microwave irradiation has been recently proposed for synthesizing HA nanostructures by calcination of sol–gel derived precursors [16]. Microwave irradiation technique has, at least two significant intrinsic advantages, one is the very fast heating rate and the second is much less processing time as compared to other techniques used for synthesizing HA. The reason for formation of HA phase by microwave irradiation could be the dielectric nature of the hydroxyl group in HA which absorb more microwave radiations. This is attributed to the change in surface energy of the powders that in turn could increase the suitable sites for nucleation [17–21].

In this work, we investigated the synthesis of nano-sized Si-HA powder by a microwave assisted chemical precipitation process.

* Corresponding author. Fax: +39 08321830130.
E-mail addresses: sanosh2001@gmail.com, sanosh.padmanabhan@unisalento.it (S.K. Padmanabhan).

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Table 1
Quantities of reactants used and the expected wt% of silicon.

Sample	$Ca(NO_3)_2{\cdot}4H_2O$ (mol)	$(NH_4)_2HPO_4$ (mol)	TEOS (mol)	Expected Si wt.%
HA	0.25	0.15	–	–
1.5Si-HA	0.25	0.132	0.0134	1.5
3Si-HA	0.25	0.114	0.0266	3
5Si-HA	0.25	0.09	0.0444	5

This method is quite capable of yielding nano-structured high purity material with a high yield and interesting microstructure. We have characterized the as-synthesized and calcined HA and Si-HA powders structurally using X-ray diffraction (XRD), scanning electron microscopy (SEM) and dynamic light scattering (DLS) techniques and spectroscopically using Fourier transform infrared (FT-IR) and EDS technique.

2. Materials and method

2.1. Synthesis of the hydroxyapatite powders

In the microwave-assisted synthesis of pure HA and Si-substituted HA, $Ca(NO_3)_2{\cdot}4H_2O$, $(NH_4)_2HPO_4$ and $Si(OCH_2CH_3)_4$(-TEOS) were used as the reagents. The amount of reagents was calculated according on the assumption that silicate would substitute phosphate. Three grades of silicate-substituted HA (Si-HA) powders were synthesized by maintaining the Ca/(P + Si) ratios fixed at 1.67, as represented in Table 1. Ammonium hydrogen phosphate $(NH_4)_2HPO_4$ was dissolves in water, the pH of the solution was kept higher than 11.0 by the addition of NH_4OH. To this appropriate amount of hydrolyzed TEOS (dil HNO_3 used as catalyst) solution was added and stirred. A 0.25 M solution of $Ca(NO_3)_2{\cdot}4H_2O$ added to the above solution and the reaction mixture was stirred for 0.5 h keeping the pH above 11 by adding NH_3. A suspension of precipitated hydroxides were obtained and irradiated with microwaves at 900 W for 0.5 h using a programmable microwave oven (Milestone MLS 1200 Mega). The resulting precipitates were filtered, dried at 70 °C overnight. The dried powders were ground using a mortar and pestle and subsequently calcined at 900 °C for 2 h in air for chemical and physical characterization.

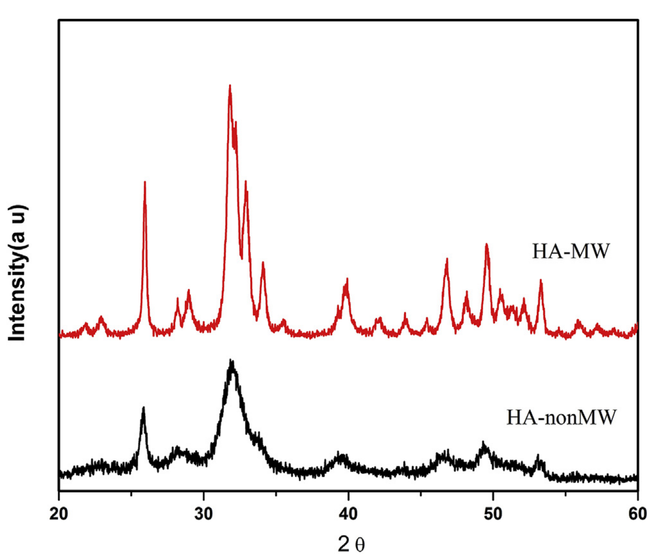

Fig. 1. X-ray powder diffraction patterns of microwaved and nonmicrowaved HA powder dried at 70 °C.

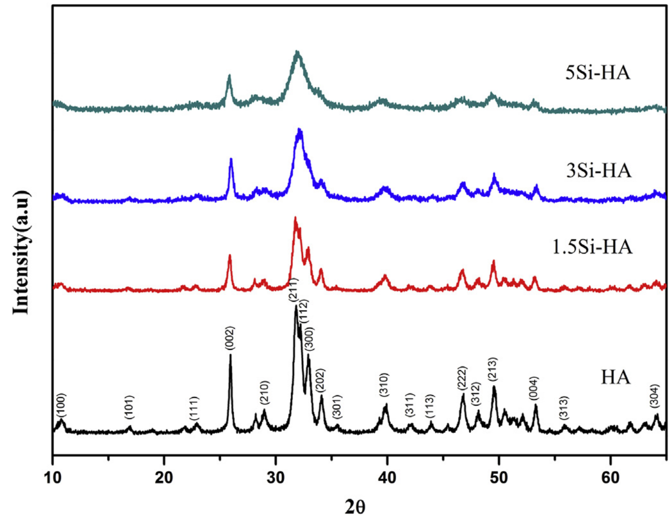

Fig. 2. X-ray powder diffraction patterns of microwaved HA and Si-HA powders dried at 70 °C.

2.2. Morphology and composition of powders

X-ray diffraction (XRD) analysis was performed using a D/max 2550V: Rigaku diffractometer, at a step size of 0.02°, scanning rate of 2° in 2 Ø/min, and a 2 Ø range from 10 to 80. The values of full width at half-maximum (FWHW) of the peak of the (002) plane, representative of the crystallites along the *c*-axis, and of the peak of the (300) plane, representative of the crystallites along the *a*-axis, were used in the calculation according Scherrer's equation [22].

$$D = (k\lambda)/(\beta \cos \theta), \tag{1}$$

where, D is the crystallite size in Å, k is Scherrer constant (0.89), λ is the wavelength of X-rays beam (1.5405 Å), θ is the diffraction angle (12.92) for the reflection (002) and (16.45) for reflection (300), and β is defined as the diffraction FWHW, expressed in radians. Determination of the lattice constants of HA and Si-HA was made by refinement of XRD data of samples calcined at 900 °C for 2 h using Unit Cell (Tim Holland and Simon Redfern) program. A dynamic light scattering (DLS) analysis (Zetasizer Nano ZS90, Malvern

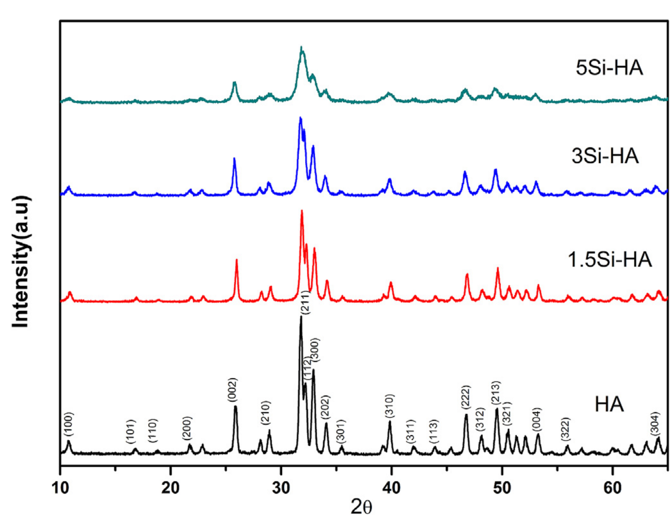

Fig. 3. X-ray powder diffraction patterns of microwaved HA and Si-HA powders calcined at 900 °C.