UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF HYDROXYAPATITE AND FLUORAPATITE NANOPARTICLES WITH DIFFERENT AMOUNTS OF FLUORIDE USING SOL-GEL METHOD

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By

POONEH KIA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

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DEDICATION

To God, who gave me life and strength

To my family. A special feeling of gratitude to my loving parents, Homa Taghavi and Gholam Hossein Kia, whose words of encouragement and push for tenacity ring in my ears, for all their love, sacrifices and faith and for their bless full prayers. To my dear sister Taraneh Kia, who is very special persons for me.

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

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April 2017

Chairman : Professor Mansor B Ahmad, PhD
Faculty : Science

Fluorapatite (FA) has been indicated as well alternative to pure hydroxyapatite (HA) in many reactions. Since the thermal decomposition and the poor corrosion resistance in an acid environment have restricted the applications of HA, as a solution, fluoride substitution in the structure of HA can improve the chemical stability and biocompatibility of HA nanoparticles. Therefore, FA nano particles can be used as a bioactive substance in the body, especially the teeth implants. Fluorhydroxyapatite (FHA) and FA nanoparticles were synthesized by adding the different amount of fluorine to the structure of HA using sol–gel method. Final products were characterized and optimized after different heat treatments of 700 °C to 1300 °C in order to improve its crystallinity. The aim of this study is to utilize sodium alginate (SA) as a bio-stabilizer in order to have the better precipitate which leads to having better crystallinity and smaller particle size. Calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, diammonium phosphate $(NH_4)_2HPO_4$, ammonium fluoride, NH_4F, were used as precursors of Ca, P and F respectively with the ratio of 1:67 Ca/P, and pH kept between 10 - 11. The presence of HA and FA phase investigated by the results of x-ray diffraction (XRD) spektroscopy which confirmed the presence of all fluoride peaks more than 0.6 wt% in the structure of FA. Fourier-transform infra-red (FTIR) spectrum showed that fluoride was substituted by hydroxyl group in the samples which contained more than 0.6 wt% fluoride, while this could be describe by two evidences; disappearing the hydroxyl group at 3600 cm^{-1} and emerged of fluoride peak at 631 cm^{-1}. Thermal gravimetric analysis (TGA) indicated that by increasing the amount of fluoride in the structure of apatite to more than 0.6 wt%, inevitably thermal stability increased. FA samples sintered at 700 ^{O}C were observed to have average sizes of 50 nm and rod like shape, which were determined by TEM and SEM, respectively. Moreover, similar samples with SA indicated smaller particle size compared to those of without SA. From another aspect, SEM and TEM, samples sintered 1300 ^{O}C indicated smaller size and finest nano rod like shape, 25

nm width and 8 nm in lengths for FA samples with SA. In conclusion, by using SA within the sol-gel method and increasing the amount of fluoride more than 0.6 wt% in the structure of HA, particle size significantly decreased and thermal stability remarkably improved.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

SINTESIS NANOPARTIKEL HIDROKSIAPATIT DAN FLUORAPATIT DENGAN KANDUNGAN FLUORIN YANG BERBEZA MELAUI KAEDAH SOL-GEL

Oleh

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Fluorapatit (FA) telah ditunjukkan sebagai alternatif yang baik kepada hidroksiapatit tulen (HA) dalam banyak tindak balas. Oleh kerana penguraian terma dan rintangan kakisan yang rendah dalam persekitaran berasid telah mengehadkan keberkesanan HA, sebagai penyesaian, fluorida yang digunakan sebagai pengganti dalam struktur HA untuk meningkatkan kestabilan kimia dan keserasianbio nanopartikel HA. Justeru, nanopartikel FA boleh digunakan sebagai bahan bioaktif dalam badan, terutamanya dalam implan gigi. Fluorhidroksiapatit (FHA) dan nanopartikel FA telah disintesis dengan menambah amaun fluorin yang berbeza kepada struktur HA dengan menggunakan kaedah sol-gel. Produk akhir diciri dan dioptimumkan selepas rawatan haba yang berbeza dijalankan pada suhu 700 ° C hingga 1300 ° C untuk meningkatkan penghablurannya. Tujuan kajian ini adalah untuk menggunakan natrium alginat (SA) sebagai penstabilbio untuk mendapatkan mendakan yang lebih baik bagi menghasilkan penghabluran yang lebih baik dan saiz zarah yang lebih kecil. Kalsium nitrat tetrahidrat, $Ca(NO_3)_2•4H_2O$, diamonium fosfat $(NH_4)_2HPO_4$, amonium fluorida, NH_4F, telah digunakan masing-masing sebagai pendahulu Ca, P dan F dengan nisbah 1:67 Ca/P, serta pH dikekalkan antara 10 - 11. Kehadiran HA dan fasa FA disiasat oleh keputusan spektroskopi pembelauan X-ray yang mengesahkan kehadiran semua puncak ion fluorida lebih daripada 0.6 wt% dalam struktur FA. Spektrum inframerah jelmaan Fourier (FTIR) menunjukkan fluorida telah digantikan dengan kumpulan hidroksil dalam sampel yang mengandungi lebih daripada 0.6 wt% fluorida, hal ini boleh diterangkan dengan dua bukti; penghapusan kumpulan hidroksil pada 3600 cm^{-1} dan kemunculan serapan fluorida pada 631 cm^{-1}. Analisis gravimetri terma (TGA) menunjukkan, dengan menaikkan amaun fluorida dalam struktur apatit lebih daripada 0.6 wt%, kestabilan haba meningkat. Sampel FA yang disinter pada 700 ^oC menunjukkan purata saiz 50 nm dan berbentuk rod, masing-masing telah ditentukan oleh mikroskopi elektron imbasan (SEM) dan mikroskopi elektron penghantaran (TEM). Selain itu, sampel yang sama dengan SA

menunjukkan saiz zarah yang lebih kecil berbanding dengan sampel tanpa SA. Dari aspek lain, SEM dan TEM, sampel yang disinter pada 1300 ^{O}C menunjukkan ukuran yang lebih kecil dan bentuk rod nano terbaik, lebar 25 nm dan 8 nm panjang untuk sampel FA dengan SA. Kesimpulannya dengan menggunakan SA dalam kaedah sol-gel dan meningkatkan amaun fluorida dalam struktur HA kepada lebih daripada 0.6 wt%, saiz partikel berkurangan secara ketara dan kestabilan haba meningkat dengan luar biasa.

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I certify that a Thesis Examination Committee has met on 13 April 2017 to conduct the final examination of Pooneh Kia on her thesis entitled "Synthesis of Hydroxyapatite and Fluorapatite Nanoparticles with Different Amounts of Fluorine using Sol-Gel Method" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science.The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

HA	Hydroxyapatite
FHA	Fluorhydroxyapatite
FA	Fluorapatite
SA	Sodium Alginate
XRD	X-ray Diffraction
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermal Gravimetric Analysis
TCP	Tricalcum Phosphate
CHA	Carbonate Hydroxyapatite
TFA	Trifluor acetic acid
FESEM	Field Emission Scanning Electron Microscope
TEA	Triethanolamine
EDX	Energy-Dispersive X-Ray Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background

Nanotechnology science currently is one of the prominent challenging areas of scientific searches due to its nanoscale level in a wide range of subjects (Paul & Robeson, 2008). Beyond these various interactions in chemical fields what are impressive are the surface areas and properties, as nanosized components play an important role by providing remarkable surface areas (Hussain et al., 2006).

Nanotechnology is greatly dependent on the size of nanoparticles, while the dimensions of particles have prominent effects on their specific features and properties (Yun et al., 2008). Irrespective of the small and tiny dimensions of nanoparticles, large surface areas to volume ratio, high energy in the relative surface, spatial confinements and decreasing the imperfections are some of the significant features of nanoparticles. Bulks and atoms materials, in contrast, are deprived of these substantial aspects (Jortner & Rao, 2002).

A tiny object which can perform like a whole unit in terms of its transport and properties is an obvious illustration of a particle that can be described in the nanotechnology field. So far as the diameter is concerned, the size of the fine particles is in the range of 100 to 2500 nanometres, while in contrast, that of ultrafine particles is mentioned to be in the range of 1 to 100 nanometres, which resembles that of nanoparticles that are measured between two nanometres (Buzea, Pacheco, & Robbie, 2007) .

At present, among the nanoparticles, synthesis of Hydroxyapatite and Fluorapatite nanoparticles has gained the attention of scientists owing to their usable properties, green methods and relatively low cost.

Hydroxyapatite has known as HA; $Ca_{10}(PO_4)_6(OH)_2$ was well perused owing to its similarities with body hard tissues and its use as a bone replaced material cause of its bone bonding ability (Shafiei, Behroozi, et al., 2012).apatite with the formula of (FA; $Ca_{10}(PO_4)_6F_2$) is also known as a bone repairing biomaterial, with antibacterial activities and significant biocompatibility features, which are also obvious illustrations of FA nanoparticles (Okazaki et al., 1999).

Hydroxyapatite demonstrates poor thermal stability by parsing into Tcp; [$Ca_3(Po_4)_2$], Tricalcum Phosphate at the thermal range further than 1200 °C, which causes problems in long term usage in ceramics and metallic implants in bones, dental roots

implants. Beyond this, Fluorapatite can keep its stability at temperatures higher than 1000 °C and up to 1400 °C (Chen & Miao, 2005).

Due to the higher solubility of Hydroxyapatite in comparison with Fluorapatite, FA indicates better stability in chemical and structural features than HA, hence, there are some parameters that are helpful to improve and control the solubility of HA by substituting the hydroxyl group (OH^-) with Fluorine (F^-). Hydroxyapatite is able to change to Fluorhydroxyapatite and consequently to Fluorapatite by replacing all Hydroxyl groups with Fluorine.

Fluorhydroxyapatite was known as FHA, $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$, in which X can be replaced by different amounts of fluorine, $0<X<1$ means the amount of fluoridation. Hence, X=0 means HA, whilst X=1 means FA. Interpolation of fluorine in the structure of pure Hydroxyapatite, or "fluoridation", diminishes the rate of solubility of HA, by keeping biocompatibility features of HA (Barinov et al., 2003).

Several methods are available for preparing HA, FHA and FA to more instant, solid state, Sol-Gel as a wet precipitation are well-known reactions for the preparation of ceramic powders. One of the most striking features is a wet chemical method named Sol-Gel method, which has many benefits such as less pH value and sintering at high temperatures, promoting chemical homogeneity in final products. Furthermore, by reducing the temperature in sintering and calcining within the sol-gel process the powders show better and higher reactivity (Darroudi, E.Hosseini, & Youssefi, 2010).

By comparing to other methods there is no doubt that sol-gel method increases hope by preparing nanosized apatite with the very fine size, in that these nanoparticles of HA and FA is well utilized in dental implants in dentistry or orthopedic applications. Therefore, by decreasing the size of nanoparticles of apatites that were prepared by so- gel, they can be easily accepted by the host tissues.

This thesis seeks to prepare, characterize and optimize; hydroxyapatite, fluorhydroxyapatite and fluorapatite with method of sol-gel. Sol-gel processing was used to synthesize the FA nanoparticles from HA powder. The advantages of the sol-gel method over other methods are precise control of composition, low processing temperature, and better homogeneity with high purity. There is no doubt that crystallinity shape and size significantly decrease by using biostabilizer of SA.

1.2 Aim of this Research

This current study aims to synthesize bio HA and FA powders within the Sol-Gel method for the evaluation of the critical method parameters and their effectiveness to control characteristic features of the ultimate HA and FA nanoparticles, such as morphology and size of crystals, and particles. These powders will be synthesized to

meet the requirements. Within different temperatures from 25 ^{O}C to 1300 ^{O}C, as an innovation Sodium alginate is used as bio-stabilize in the solution as a green sol-gel method, in order to compare the different crystallinity sizes.

1.3 Problem Statement

Hydroxyapatite has a high rate of solubility that can increase the rate of decay in the biological system, which is a major problem in the structure of HA. On the other hand, poor stability at high temperatures and easy corrosion in acidic fields also cannot be ignored as they place many application limitations in orthopedics and dentistry, while Fluorapatite, compared to HA has lower solubility and better stability in terms of structure and chemically. Modulating the degree of Fluorine replacement in the structure of HA allows for the control of the solubility of the apatite. (Kim, Kim, & Knowles, 2004)

Much of the research has focused on the manufacturing FA particles by precipitation techniques or films within thermal spraying methods. Unfortunately, the properties of matter and qualities of the particles and films have proven to be unsatisfactory because of the forming byproducts or because of some technical errors. In this regard, the sol-gel approach has often been adopted to overcome these difficulties. Whilst, the sol-gel technique has been suggested as a promising approach to address several of these problems. Medically, the application of materials and devices with sol-gel coatings is already becoming widespread and is expected to growth in the future years for application within implant materials, drug-delivery systems, grafting of bone and materials with biogenic features with scaffolds and biologically active membranes (Ben-Nissan & Choi, 2006).

1.4 Objectives

The main objective is to:

As an innovation synthesizing, optimization and characterization of HA and FA within Sol-Gel method by adding sodium alginate into their structure as a bio green stabilizer. Green synthesis method in the producing FA nanoparticle can be an alternative which should be conducted in the first main part of sol-gel method by adding natural biopolymer such as Sodium alginate as a biostabilizer for having better precipitate which lead to have fine particle size.

The specific objectives are to:

(1) Synthesize and optimize the FA nanostructures by adding the different amount of fluorine within the structure of HA which produced within the method of the sol-gel.
(2) Characterize and investigate the size of the particles and morphology of the HA, FA by sol-gel method under thermal treatment range of 700 ^{O}C for

calcination and 1300 ^{O}C for sintering and comparing the different shapes and sizes between HA and FA by using bio-stabilizer of SA.

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