Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Facile microwave-assisted synthesis of tungsten-doped hydroxyapatite nanorods: A systematic structural, morphological, dielectric, radiation and microbial activity studies

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ARTICLE INFO

Keywords:
Hydroxyapatite
X-ray diffraction
FT-Raman spectroscopy
FE-SEM, radiation studies
Dielectric properties
Antimicrobial activity

ABSTRACT

Herein we report a low temperature, rapid microwave-assisted synthesis of pure and tungsten (W) doped hydroxyapatite (HAp) nanorods. X-ray diffraction study confirmed the good crystalline nature of synthesized product and various key parameters such as: grain size, dislocation density, lattice strain, degree of crystallinity and lattice parameters were estimated. The average value of grain size is found to be in the range of 11–32 nm and the highest degree of crystallinity was observed for 40 wt% W doped HAp (viz. ~ 67.3%). Functional groups and modes of vibrations were analyzed by FT-IR and FT-Raman spectroscopic studies. Morphology and elemental compositions of synthesized nanostructures were analyzed by FE-SEM/EDX measurements that confirms the formation of very low dimension nanorods (diameter < 5 nm)/presence of dopant. Dielectric constant and ac electrical conductivity values are found to be enriched by doping. Gamma linear absorption studies were carried out using Cesium-137 (^{137}Cs) radioactive source and shows an enhancement in radiation absorption with an increase of doping which makes it useful in radiation shielding. Furthermore, the synthesized nanorods were applied to test their catalytic activity for methyl orange-removal in the presence of bacteria. The W doped HAp exhibited a great catalytic activity in presence of *Enterococcus feacalis* bacteria which indicates its applications in waste water treatment.

1. Introduction

The research and development on calcium orthophosphates based materials are in colossal demand due to their biomedical applications as they contain similar components like: human bones and teeth. Hydroxyapatite (HAp) is one of the excellent non-toxic materials from such category with the exceptional biological rejoinder and applied in orthopedics, dentistry, plastic surgery, neurosurgery as bone cement material and also has further applications as catalyst, gas sensor, water purification, luminescence, production of fertilizers, hold back the growth of cancer cells and drug carrier [1–8]. Various dopants has been tried to modify the key properties of HAp like: biological, mechanical strength, dielectric and optical etc. for the above mentioned applications [9–15]. To achieve enhanced properties the synthesis of pure and doped HAp nanostructures has been carried out using different techniques [7,16–22]. Among all applied techniques the microwave-assisted technique is found to be superior in many ways to achieve improved and homogeneous morphology nanostructures of high crystallinity [23–29]. According to the available literature only one report is available on W doped HAp so far [30]. In this report the authors have applied the ball milling technique using HAp and WO_3 (up to 0.5%) is used as a W source as starting materials and studied the bioactivity and polarizability properties. The use of HAp and WO_3 for the preparation of W doped HAp by ball milling technique seems to be costly and time taken. In recent past the doping of W has also been tried in many applicable materials such as TiO_2, VO_2, composites of nickel ferrite to enhance their properties [31–33]. Methyl orange (MO) is one of the most abundant waste materials worldwide. It is toxic, mutagenic and carcinogenic to both aquatic animals and humans. It is used in textile and paper industries; however, it is highly reactive and

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http://dx.doi.org/10.1016/j.ceramint.2017.08.009
Received 1 July 2017; Received in revised form 28 July 2017; Accepted 1 August 2017

difficult to treat. Moreover, many researchers have reported the decolorization of different textile dyes by a variety of microorganisms [34,35]. Biological methods, biosorption and biodegradation, have been investigated to have good potency for the removal of dyes [36]. Biodegradation can be interpreted as the uptake of toxic materials by living cells. Conversely, biosorption can be known as the passive uptake of toxic materials by dead/inactive biological cells. Microbial biosorbents have advantages like high biosorption efficiency, rapid, steady state attainment, less cost and better particle mass transfer. A new development in this area is the combined action of microbial source with nanoparticles in order to enhance dye removal [37]. Herein, the authors aim is to synthesize the nanostructured ceramic of pure and 1, 5, 10. 20, 30 and 40 wt% W doped HAp using commercially available low cost materials by microwave-assisted [23,24,38]. The synthesized nanostructures were characterized for various properties such as structural, vibrational, morphological, compositional, and applications like dielectric, radiation detection and bioactivity and discussed.

2. Experimental details

2.1. Synthesis

Commercially available calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], di-ammonium hydrogen phosphate [$(NH_4)_2HPO_4$], cetyltrimethyl ammonium bromide (CTAB) as surfactant, ammonium hydroxide as a pH adjuster, Sodium tungstate dihydrate ($H_4Na_2O_6W$) materials of high purity were bought from Sigma Aldrich. The synthesis of pure and 1, 5, 10, 20, 30 and 40 wt% W doped HAp was achieved as per previously reported method [8].

2.2. Characterization techniques

To observe the effect of W doping on structural properties of HAp, the powder X-ray diffraction measurements were done using a Shimadzu LabX XRD-6000, X-ray diffractometer having CuKa (λ = 1.5406 Å) radiation at ambient conditions and the collected data was studied by Shimadzu software attached with XRD and pdf2 library.

For functional group and vibrational modes analyses the FT-IR and FT-Raman spectra were recorded using THERMO SCIENTIFIC, DXR FT-IR and FT-Raman spectrometer in the wavenumber range of 4000–400 cm^{-1} and 3500–100 cm^{-1}, respectively. The 532 nm laser excitation source and 5 mW power with estimated resolution ~ 5.1–8.3 cm^{-1} was used to record the FT-Raman spectra. The elemental composition and nanostructure morphology were analyzed by field emission scanning electron microscope (FE-SEM) equipped with Energy-dispersive X-ray spectroscopy (EDXS) (JSM-7500 F; JEOL-Japan). A Keithley 4200-SCS system is used to measure the capacitance, loss tangent, impedance in the frequency range of 3 kHz–10 MHz at ambient conditions to study the effect of W on dielectric constant, loss and ac conductivity of HAp. For radiation study we have used a NaI detector 1.5 PX 1.5/2.0 IV (REXON, components, Inc. USA) attached with universal computer spectrometer UCS-20 and the prepared nanostructures were studied using gamma ray source (Cs^{137}) of energy 662 keV for duration about 100 s.

2.3. Antimicrobial activity of pure and W doped HAp nanorods

Methyl orange (MO) and *Enterococcus feacalis* bacteria used in this work were arranged from a biological laboratory at King Khalid University.

2.3.1. Microorganism and culture media

Bacteria used in this study is *Enterococcus feacalis* strain kilany MO (GenBank accession number: KY780590). Nutrient broth and nutrient agar media were used for bacterial culture for 24 h at pH 7, 100 rpm and 30 °C and preserved at 4 °C. All used media and tools were autoclaved at 121 °C for 15 min.

2.3.2. Enhancement of MO biosorption

2.3.2.1. Decolorization of live and dead bacterial cells. Bacterial culture was grown overnight in MO supplemented-nutrient broth, centrifuged at 6000 rpm for 5 min and then washed three times with KK_2 buffer (6.5 mM KH_2PO_4, 3.8 mM K_2HPO_4, pH 6.2). The volume of the bacterial suspension is then adjusted to a density of 10^{12} cells/ml (assuming that an OD_{650} of 0.1 corresponds to 10^8 cells/ml). Cells are heat-killed at 70 °C for 10 min [39] and added to 100 ml NB media containing 100 mg/ml MO. Consequently, live bacterial cells inoculated to another 100 ml NB media containing 100 mg/ml MO. Both flasks were incubated at 37 °C. Aliquots of 3 ml of each flask withdrawn at zero time, 24 h and 48 h and checked at 464 nm.

2.3.2.2. Enhancement of decolorization. An approximately 0.25 g pure and W doped hydroxyapatite nanoparticles were slowly stirred at room temperature after adding 10 ml of both live and dead bacterial culture, separately and an aliquot was immediately withdrawn at zero time, then the remaining samples were left to incubate at 24 h and 48 h. Abiotic control was prepared by diluting 10% (v/v) MO solution with 90 ml phosphate buffer solution (pH 7). Experiments were performed in triplicate. The extent of decolorization of MO was calculated as follows: -

$$\%\text{Decolorization} = (\text{Ao} - \text{At})/\text{Ao} \times 100$$

where A_o refers to the initial absorbance of sample and A_t refers to absorbance at different time intervals at 464 nm [40].

3. Results and discussion

3.1. X-ray diffraction analysis

The recorded X-diffraction patterns for all nanostructures with *h*, *k*, *l* indexing are shown in Fig. 1, which proves that the prepared nanostructures are well crystalline and possess Hydroxyapatite phase predominantly with the hexagonal crystal system even at higher doping concentration. The refinement of XRD data was found to be well matched with the reported data JCPDS# 09–0432. However, at higher concentration doping of W, some peaks of WO_2 (JCPDS# 11-0693) were observed.

For calculating the lattice parameters like a, b, c and unit cell volume V of all nanostructures, the following equation is used [41]: $\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$, and $V = 0.866a^2c$, here d is distance between

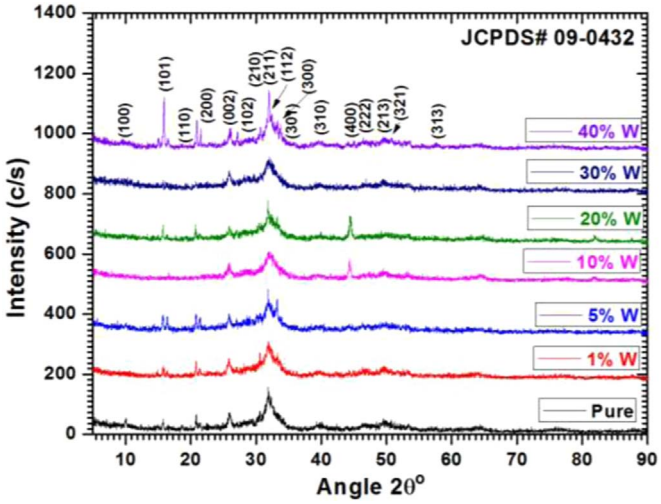

Fig. 1. XRD pattern of undoped and W doped HAp nanorods.