



Facile microwave-assisted synthesis of Te-doped hydroxyapatite nanorods and nanosheets and their characterizations for bone cement applications



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ABSTRACT

In this work, the authors have fabricated the nanorods and nanosheets of pure and Te-doped HAP with different Te concentrations (0.04, 0.08, 0.16, 0.24 wt%) by microwave-assisted technique at low temperature. The crystallite size, degree of crystallinity and lattice parameters are calculated. FE-SEM study confirms that the fabricated nanostructures are nanorods of diameter about 10 nm in undoped and at low concentration of Te doping. However, at and higher concentration, it becomes nanosheets of about 5 nm thickness. X-ray diffraction, FT-IR and FT-Raman studies shows that the prepared products are of HAP and Te has been successfully incorporated. From EDX the Ca/P molar ratio of the pure HAP is about 1.740, while this ratio for 0.04, 0.08, 0.16, 0.24 wt% Te doped is about 1.53, 1.678, 1.724, 1.792, respectively. Crystallite size was found to be increased with Te doping from 15 nm to 62 nm. The value of dielectric constant is found to be enhanced at higher concentrations of Te. The values of linear absorption coefficient were also determined and show that the prepared material with Te doping is more absorbable than pure and will be highly applicable in radiation detection applications. Furthermore, the antimicrobial potential of pure and Te doped HAP was examined against some Gram- negative and positive bacteria and fungi by agar disk diffusion method. The results demonstrated that the antimicrobial activity of Te doped HAP is stronger than that of pure HAP where it exhibited the highest activity against *Bacillus subtilis* > *Candida albicans* > *Shigella dysenteriae*.

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1. Introduction

Hydroxyapatite (HA) is an excellent non-toxic material with uncountable applications in the field of biomedical as well as optoelectronics. It has many applications in retarding the multiplication of cancer cells, as implant biomedical materials in orthopedic and dental treatments, prostheses, repair of bone defects, bone augmentation, coating the metallic implants and filling of bone gaps and shows excellent biocompatibility, bioactivity osteoconductivity and affinity etc. [1–11]. It was also used as catalyst in chromatography or gas sensor, water purification, luminescence, fertilizers production and drug carrier [12,13]. It is well known that HAP has a structure that facilitate some ion incorporations such as K^+ , Ag^+ , Na^+ , Mn^{2+} , Ni^{2+} , Cu^{2+} , Co^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Cd^{2+} , Y^{3+} , La^{3+} , Fe^{2+} , Zn^{2+} , Mg^{2+} , Ce^{3+} , Al^{3+} , P, Si, V, Cr, (CO_3^{2-}) and F^- , Cl^- , O^{2-} , OH^- , Br^- can substitute Ca^{2+} , (PO_4^{3-}) and (OH^-) ions, respectively [14–21] in to its crystalline lattice that results in remarkable change of mechanical and biological properties. HAP crystallize in hexagonal

crystal structure with lattice parameters $a = b = 0.9418$ nm, $c = 0.6884$ nm with unit cell volume $V = 0.5288$ nm³ [22–24]. Several reports are available on the preparation of HAP nanostructures by different methods such as chemical co-precipitation, sol-gel process, spray-pyrolysis, hydrothermal synthesis, emulsion or micro-emulsion routes, gel method, microwave [25–32]. The sol-gel method is useful for the synthesizing of HAP, because this method has many advantages, containing high product purity and low synthesis temperature [23,26,33, 34]. However, the microwave technique has the advantage of homogeneous internal and volumetric heating at rapid rates [35–41] and found to be better than conventional heating to achieve high crystalline nanostructure materials.

As per the current available literature there is no study has been made on Te doped HAP so far. However, the Te/TeO₂ has been widely doped in different kind of materials such as SnO₂, ZnO, glassy systems etc. and found to enhance their key properties for future device applications [42–45]. Hence, due to such influence of Te/TiO₂ on the key properties we have also aimed to fabricate the nanostructures of HAP with different concentrations of Te-doping (0.04, 0.08, 0.16, 0.24 wt%) via a microwave heating process - a rapid and cost effective route [35,36,

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46] and study its effect on crystallinity, crystalline structure, phase composition, morphology, vibrational, dielectric and radiation detection and biomedical properties etc. and the obtained results are discussed here.

The increases of morbidity and mortality caused by pathogenic bacteria and fungi are very high and researchers worldwide are searching new alternative therapies and new drugs to reduce these infections. New therapeutic and prophylactic strategies are urgently required to prevent microbial infection. HAp represent a new generation of antimicrobial materials [47–51]. Therefore, it is expected that a hybrid material constituted of Te doped hydroxyapatite will exhibit improved mechanical, biological, and antimicrobial properties, thus making it an excellent candidate for numerous biomedical applications.

2. Experimental details

2.1. Materials

For the fabrication of Te doped HAp nanostructures, Calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], ammonium hydrogen phosphate ADP ($\text{NH}_4\text{H}_2\text{PO}_4$), cetyltrimethylammonium bromide (CTAB), ammonium hydroxide (NH_4OH) and potassium tellurite (K_2TeO_3) were purchased from Sigma Aldrich and used without further purifications.

2.2. Synthesis of Te doped HAp nanostructure

For the synthesis of undoped and Te doped HAp nanostructures, we have used the following procedure: 1) In 100 ml of double distilled water, the calculated amount of 0.5 M calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$] and 0.3 M ammonium hydrogen phosphate ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) were dissolved separately in two beakers by continuous stirring (800 rpm) at constant temperature i.e. 90 °C. In the prepared solution of Calcium nitrate tetrahydrate, ADP was added gradually. Further a surfactant named cetyltrimethyl ammonium bromide (CTAB) was added to the prepared solution for controlling the structure morphology of HAp. To set the pH about 10 of the readied solution we have added the ammonium hydroxide by continuous stirring for at least 1 h and one more hour stirring was done to achieve the white precipitate. The different concentrations (0.04, 0.08, 0.16, 0.24 wt%) of Te doping have been done in the prepared solution in terms of potassium tellurite. The finally prepared solutions were subjected to microwave irradiation to get the complete synthesis of undoped and Te doped HAp. For microwave irradiation the Anton Paar microwave [Multiwave Pro 1500 W (IEC 705)] operated at fixed power ~700 watt and temperature 145 °C for 20 min has been used to have fast and rapid thermal shock to form the exact crystalline phase of HAp. At the end of the microwave process all the prepared precipitates were cleaned using distilled water and alcohol for several times to remove any unwanted impurity. Finally the as-prepared powders were dried at 100 °C for 24 h.

2.3. Characterization methods

X-ray diffraction patterns of undoped and Te doped HAp nanostructure samples were carried out using a X-ray diffractometer of Shimadzu LabX XRD-6000 with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation, operated at 30 mA and 40 kV at the scan rate of $0.2^\circ/\text{m}$ over the angular range of 10° to 90° at 300 K. The recorded XRD data was analyzed using the Shimadzu software attached with XRD and pdf2 library for the matching process. The morphology of the fabricated nanostructures was studied using a field emission scanning electron microscope (FE-SEM) (JSM-7500 F; JEOL-Japan). FT-IR spectra was also recorded using THERMO SCIENTIFIC, DXR FT-IR spectrometer by KBr pallet method in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$. The FT-Raman spectra was also recorded using a THERMO SCIENTIFIC, DXR FT-Raman spectrometer accompanied with microscope in the wavenumber range of $1500\text{--}50 \text{ cm}^{-1}$, the excitation wavelength was 532 nm and laser power 2 mW. The dielectric constant, loss and ac conductivity measurement were

performed using Keithley 4200-SCS characterization system in the high frequency range from 3 kHz to 10 MHz at room temperature. The linear absorption coefficient was determined by measuring the values of the initial intensity of radiation before attenuation (I_0) and the final intensity after attenuation (I) using NaI detector 1.5 PX 1.5/2.0 IV (REXON, components, Inc., USA) attached with universal computer spectrometer UCS-20. In this measurement, we have placed the detector in such way between radioactive point source and the detector window so that the detection of any radiation coming directly from the source and scattered from the surroundings can be minimized, to remove the scattered radiation we have designed Lead collimator. The gamma ray source (Cs-137) of energy (662 keV) and (Am-241) of energy (59.5 keV) were used for irradiating the samples for 100 s duration of time at room temperature.

The antimicrobial activity of pure hydroxyapatite and tellurium-doped hydroxyapatite was detected by agar disk diffusion method using Müller-Hinton agar medium [32]. All materials were steam sterilized at 115 °C for 15 min. A volume of 15 ml sterile culture medium was evenly inoculated with Gram-positive bacteria (*Bacillus subtilis*, *Staphylococcus aureus* and *Micrococcus* sp.), Gram-negative bacteria (*P. aeruginosa*, *Klebsiella* sp. and *Shigella dysenteriae*) and *Candida albicans*. Twenty-five mg disks of pure hydroxyapatite and tellurium-doped hydroxyapatite were put onto the Petri dishes surface. Then after the Petri dishes were incubated at 37 °C for 24 h. The inhibition zones were measured in millimeter and the assay was performed in triplicate.

3. Results and discussion

3.1. Nanostructure structure analysis

To confirm the nanostructure morphology and elemental composition of pure and Te-doped HAp the FE-SEM/EDS micrographs/patterns were captured and shown in Fig. 1. The presence of Te has been confirmed from EDS pattern. SEM analysis confirms that the fabricated nanostructure of pure and 0.04% Te-doped is nanorods of diameter about 10 nm, however for 0.08, 0.16 and 0.24% Te doped it is nanosheets of thickness about 5 nm. The Ca/P molar ratio of the pure HAp is about 1.740, while this ratio for (0.04, 0.08, 0.16, 0.24 wt%) Te doped is about 1.53, 1.678, 1.724 and 1.792, respectively. The change in the ratio was observed with the addition of Te, this is also may be due to ionic substitution and may attributed to crystal defect. The obtained results are in good agreement with the earlier reports [52].

3.2. Phase and crystal structure analyses

Fig. 2 shows the recorded X-ray diffraction patterns of all the prepared nanostructures. The X-ray diffraction data was used to confirm the crystalline structure, crystalline phase and crystallinity of pure and Te-doped HAp nanostructures. From this figure, it is clear that the prepared nanostructure are well crystalline and has Hydroxyapatite phase, with hexagonal crystal structure and found in good correlation with JCPDS# 09-0432 and also confirmed from the peaks observed in all diffraction patterns correspond to the (100), (002), (211), (300), (202), (310), (222), (213), (004) and (304) planes, respectively. The main phase of Hydroxyapatite was observed in all the samples however with Te doping some peaks of TeO_2 (JCPDS# 11-0693) were also observed due to doping at higher concentrations only. The diffraction peaks of TeO_2 confirm the inclusion of Te in the crystalline matrix of HAp.

The lattice parameters (a and c) and unit cell volume (V) of the prepared nanostructure were determined using the following relations [53]:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

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