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Cobalt Ions Doped Bioactive Ceramics for Biosensor Biomedical Applications

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ABSTRACT

Cobalt ions doped hydroxyapatite (Co-HAp) was synthesized by ultrasonication assisted co-precipitation route. The phase of HAp was confirmed by XRD analysis. The crystallite size of doped sample was reduced (28%). The functional groups of HAp were confirmed by FTIR and Raman analysis. Cobalt ions doped samples were showed magnetic behavior. In addition, optical properties of the samples were also carried out. Hence, cobalt ions doped samples could be an excellent candidate in biosensor and biomedical fields.

Key Words: Bioceramics, Cobalt, Raman, Magnetic

INTRODUCTION

Nanostructure materials are very attractive due to their unique chemical and physical properties and have found potential applications in nanoelectronic devices, catalysts, and drug delivery and release kinetics. During the past few years, the exploration of nano materials and its properties. They lead to functionalized material arrays and transport phenomena at nanometric scale [1, 2]. Hydroxyapatite [HAp, $\text{Ca}(\text{PO}_4)_3(\text{OH})$] is a bioceramic analogous to the mineral component due to its nontoxicity excellent biocompatibility and bioactivity. HAp exhibits strong surface absorption ability because of its surface functional groups and special chemical constitutions [3]. Recently, it has received considerable attention as a chemical gas sensor due to its peculiar properties such as presence of large surface phosphate groups which interacted with the gas molecules to be sensed highly and capability to exchange ions [4]. Functionality of HAp can be realized by addition of metal ions to the structure of HAp [5]. Metal ions might be incorporated in hydroxyl site, phosphate site or calcium sites of HAp in order to improve its properties [6]. Numerous studies were reported that calcium ions can be replaced by various metal ions which could modify the functionality of HAp [7-9]. In the present work, HAp and cobalt doped HAp were synthesized by ultrasonication assisted wet chemical synthesis to examine for physiochemical properties.

MATERIALS AND METHODS

Materials

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) from Merck, diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) from Merck, cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) from Fisher scientific and ammonia solution (25%) from Merck.

EXPERIMENTAL METHOD

Synthesis of HAp

The calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and diammonium hydrogen phosphate were used as a calcium (Ca^{2+}) and phosphate (PO_4^{3-}) source respectively. The calcium and phosphate sources were taken as a precursor in the ratio of 1:0.6 respectively and double distilled water was used as a solvent. In typical synthesis, the calcium nitrate tetrahydrate solution was drop wise added to phosphate solution under vigorous stirring and ultrasonicated at pH (10) using ammonia solution. After the completion of reaction, the precipitate was washed many times using double distilled water to remove the excess nitrates present on it. The white precipitate was dried in vacuum condition in 80°C and mechanically grinded and the obtained powder was named as HAp [10-12].

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Synthesis of cobalt ions doped HAp

To prepare cobalt ions doped HAp the above mentioned HAp synthesis procedure was followed. To maintain the stoichiometry ($\text{Co}_x\text{Ca}_{10-x}(\text{PO}_4)_6\text{OH}_2$), the cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as a cobalt ion source (0.05M). After completion of reaction the sample was labeled CHAp.

Characterization methods

The phase confirmation of the samples was performed by X-ray powder diffraction method using analytical diffractometer (PANalytical) with $\text{CuK}\alpha = 1.54 \text{ \AA}$ radiation. The data was collected in 2θ range of (10° to 80°) with a step size of 0.040. Infrared spectrum was collected in the range of 4000 cm^{-1} to 400 cm^{-1} using FTIR spectrometer (JASCO FT/IR6300) using KBr pellet method. Raman studies were performed at 1064 nm . The optical properties of the samples were studied using UV-Vis spectrophotometer in the range of 200 nm – 800 nm using Jasco 750 series in Diffuse Reflectance Spectroscopy (DRS).

RESULTS AND DISCUSSION

X-Ray Diffraction analysis

The XRD spectra of the samples were shown in Fig.1. The phase purity of the samples was well matched with JCPDS data (09-0432). The peaks at 25.87° , 31.94° , 32.91° and 33.96° and their corresponding planes (002), (211), (112) and (300) unaltered. The diminishing of peak intensity was due to incorporation of cobalt ions that contract lattices and which leads to decrease in the crystallinity. Cobalt ions were occupied the interstitial sites of HAp could be due to lesser radius of Co^{2+} ions than Ca^{2+} ions [19-21].

FTIR analysis

FTIR spectra of HAp and doped samples were shown in Fig.2. The spectrum was recorded in the region of 4000 cm^{-1} – 400 cm^{-1} . The vibrational mode ν_4 of $(\text{PO}_4)^{3-}$ was obtained at 567 cm^{-1} , 603 cm^{-1} and 633 cm^{-1} which correspond to hydroxyapatite [13]. The O-H band was observed at 3427 cm^{-1} due to the presence of H_2O molecules. On doping of Co^{2+} ions, the phosphate band shifted to lower wavenumber. The band 633 cm^{-1} was associated to OH bending mode [14]. The absorption bands were appeared at 1458 cm^{-1} and 872 cm^{-1} which corresponds to ν_3 and out-of-plane ν_2 modes of CO_3^{2-} [15].

Raman analysis

Raman spectra of HAp and doped samples were shown in Fig.3. Raman vibrations of phosphate, carbonate and hydroxyl ions were observed in apatite at 400 cm^{-1} . The characteristic peak of $\nu_1(\text{PO}_4)$ band was found at 963 cm^{-1} . The

mode $\nu_1(\text{PO}_4)$ was associated to the total symmetric stretching mode of free tetrahedral phosphate ions [16]. The peak was observed at 1045 cm^{-1} which correspond to asymmetric stretching mode of $\nu_3(\text{PO}_4)$. The peak at 586 cm^{-1} was attributed to the bending mode of PO_4 group.

Diffuse Reflectance UV-Vis Analysis

The Diffuse reflectance UV-Vis spectra of the HAp and doped samples were showed in Fig-4. The band was observed in the region of 240 nm for HAp could be due to charge transfer of Ca^{2+} ions to O^{2-} ions. In the case doped sample, showed a broad absorption band (471 nm to 686 nm) due to the exchange of cobalt ions [17-19].

Photoluminescence

Fig. 5 showed the emission spectra of HAp and doped samples. The emission spectra were exhibited a shoulder peak in the region from 350 nm to 370 nm was due the weak crystal field. The broad emission band from 385 nm to 415 nm and intense peak observed at 396 nm . The enhanced PL intensity was observed due to the electron-hole pair recombination. The small humps were observed at 336 nm and 467 nm could be due to defects in the sample [20,21].

CONCLUSIONS

Cobalt based HAp was synthesized by ultrasonication assisted wet chemical synthesis. X-ray diffraction confirmed the phase purity and crystallinity of the samples. Furthermore, FTIR and Raman analysis were confirmed the presence of hydroxyl, carbonyl and phosphate groups. Enhanced PL and UV absorbance were observed on cobalt doped samples. Hence, the doped samples could be an excellent candidate in biosensor and biomedical fields.

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Table 1

IR Frequency (cm ⁻¹)	Assignments
469	$\nu_2(\text{PO}_4)^{3-}$
567, 603, 633	$\nu_4(\text{PO}_4)^{3-}$
872	$\nu_2(\text{CO}_3)^{2-}$
1065	$\nu_3(\text{PO}_4)^{3-}$
3577	$\nu_3(\text{OH})$
1458	$\nu_2(\text{CO}_3)^{2-}$

Figure 1: XRD Spectrum, (a) HAp (b) 0.05 Co-HAp.

Figure 2: FTIR Spectra, (a) HAp (b) 0.05 Co-HAp.

Figure 3: Raman Spectra, (a) HAp (b) 0.05 Co-HAp.

Figure 4: UV-Vis Spectra, (a) HAp (b) 0.05 Co-HAp.

Figure 5: PL Emission Spectra, (a) HAp (b) 0.05 Co-HAp.