Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S324-S328

ASIAN JOURNAL OF CHEMISTRY

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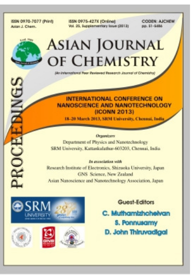

ISSN 0970-7077 (Print)
Asian J. Chem.

ISSN 0975-427X (Online)
Vol. 25, Supplementary Issue (2013)

CODEN: AJCHEW
pp. S1-S486

ASIAN JOURNAL OF CHEMISTRY
(An International Peer Reviewed Research Journal of Chemistry)

PROCEEDINGS

INTERNATIONAL CONFERENCE ON NANOSCIENCE AND NANOTECHNOLOGY (ICONN 2013)
18–20 March 2013, SRM University, Chennai, India

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SRM University, Kattankulathur-603203, Chennai, India

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Synthesis and Structural Characterization of Hydroxyapatite/TiO_2 Nanocomposite Coatings for Potential Biomedical Applications†

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AJC-12866

Hydroxyapatite ceramics have been recognized as substitute materials for bone and teeth in orthopeadic and dentistry fields due to their chemical and biological similarity to human hard tissue. Sol-gel technique has been developed and employed to prepare various materials because of easy control of homogeneity of the final product and low temperature synthesis. Hydroxyapatite/titania nanocomposites of different ratios are successfully synthesized by a simple sol-gel dip coating method. The coatings were done under controlled dipping and heat treatment processes. Further to heat treatment of the prepared nanocomposites, phase pure hydroxyapatite and TiO_2 were found to be well developed and confirmed from the XRD studies. The SEM analysis of hydroxyapatite/TiO_2 nanocomposite coatings shows the variation in morphology as a consequence different TiO_2 concentration. EDAX analysis confirmed the presence of Ca, P, Ti and O. The FTIR studies established the presence of functional groups.

Key Words: Hydroxyapatite, Titanium dioxide, Nanocomposites, Coatings, XRD, SEM.

INTRODUCTION

Increasing demands for smarter and smaller products call for the development of multiphase and multifunctional materials. In recent years, with the growing necessity for biocompatible materials, hydroxyapatite (HAp) with the composition $Ca_{10}(PO)_4(OH)_2$, has received extensive attention for its potential use as a bone filler and implant material due to its excellent biocompatibility, close chemical and crystallographic structure with the mineral phase of natural bone[1]. Successful bone fixation has been shown to be related to the surface morphology and composition of the material. Along with composition, the evaluation of morphological characteristics of hydroxyapatite such as shape, size and uniform size distribution of particles play a vital role in determining is mechanical, chemical and biological activities[2].

The mechanical properties of hydroxyapatite are poor, especially in wet environment, alarming their limitations for use in heavy-loaded implant such as artificial bones or teeth[3]. Thus, regardless of their favourable biological properties, the poor mechanical properties of hydroxyapatite bioceramics leads to instability and unsatisfactory performance of the implant or scaffold in the presence of body fluids and under local loading[4]. The best way to overcome these mechanical limitations is to use bioactive hydroxyapatite as part of ceramic/metal composites so as to achieve both necessary mechanical strength and bioactive properties[5]. In general, the creation of nanostructures of ceramic materials with grain/particle size less than *ca.* 100 nm can significantly improve the bioactivity of the implant and enhance the osteoblast adhesion[6]. However, a good understanding of the composite coating formation mechanism and structure characterization is necessary to contribute considerably for the development of the reinforced bioceramic coatings[7]. Hence understanding the synthesis and formation mechanism of hydroxyapatite composite thin films has attracted much attention in recent times, as such coatings are expected to improve the biocompatibility, bioactivity and also the mechanical strength of the implants[8].

The present work aims at preparing a composite thin film of hydroxyapatite in a TiO_2 matrix by sol-gel dip coating process and to study the influence of titania on the microstructural properties. Since there are not many reports that link the morphological changes with the corresponding properties of the bioactive coatings, the present study mainly focuses on the nanostructural morphological variations with respect to

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†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

TiO_2 concentration. The hydroxyapatite/TiO_2 composites are prepared on optically plane surfaces with a possibility to further extend the studies to understand the mechanical and adhesion property for bioactive glasses and borosilicate glasses used for biomedical applications.

EXPERIMENTAL

Preparation of hydroxyapatite colloidal solution: Hydroxyapatite sol was prepared using calcium nitrate tetra hydrate [$Ca(NO_3)_2{\cdot}4H_2O$] and orthophosphoric acid [H_3PO_4] as calcium and phosphorus precursors, respectively. Stoichiometric hydroxyapatite was prepared by dissolving 1.67 M calcium nitrate in 2-methoxy ethanol and stirred for 1 h. 1 M orthophosphoric acid was added drop wise to the above solution under vigorous stirring to maintain the Ca/P ratio as 1.67. In order to avoid the formation of precipitates, few drops of HNO_3 was added to the mixture. After 2 h of stirring, a transparent solution was obtained and this was kept for 24 h with mild stirring to increase the viscosity of the sol to prepare thin films.

Synthesis of TiO_2 solution: Titanium tetra isopropoxide (TTIP) (Aldrich chemicals, USA) was used as a titanium precursor. Since titanium alkoxide used in this study is highly unstable in air, the chelated TiO_2 sol was prepared using acetyl acetone as a ligand and HCl as the acid catalyst. Initially 1 M TTIP was mixed with 2-methoxy ethanol. The 0.5 M acetyl acetone and 0.35 M HCl was added drop wise to the above solution under vigorous stirring. Finally, required amount of water was added slowly under stirring to obtain a molar ratio of 2-methoxy ethanol:TTIP:acetyl acetone:H_2O as 40:1:1:1. After vigorous stirring for 1 h, the resultant transparent solution was kept for 24 h with mild stirring, for further use in film preparation. Both the experiments were carried out at room temperature.

Preparation of hydroxyapatite/TiO_2 nanostructured composite coatings: Optically plane glass slides were used as substrates and cleaned with chromic acid followed by NaOH solution to remove oil, grease *etc*. from the surface. The cleaned substrates were agitated with ultrasonic agitator using acetone and vapor degreased with isopropyl alcohol. Finally the glasses were dried in an oven at 100 ºC for 1 h before coating the thin films. Hydroxyapatite/TiO_2 composite solutions with variable hydroxyapatite/TiO_2 concentrations were prepared by mixing the required amounts of as-prepared hydroxyapatite and TiO_2 solutions. Five different hydroxyapatite/TiO_2 concentrations were prepared in the present study.

Thin films of hydroxyapatite/TiO_2 were deposited onto the glass substrates using dip coating method. The substrate was dipped into the solution and withdrawn at a constant rate. The immersion time was also varied for each dipping and after each immersion the substrates were exposed in air for 0.5 h for hydrolysis (elimination of water molecules). The exposed substrates were then kept in oven at 180 ºC for the removal of the solvent. Again the substrates were kept in open atmosphere for 0.5 h. The substrates were again dipped in the solution and procedure was repeated until the required film thickness was obtained. Dipping and withdrawal speeds were maintained for good homogeneity of obtained films. The prepared thin films were then annealed at 500 ºC in air.

Characterization: The prepared samples were structurally characterized by X-ray diffraction analysis [RIGAKU X-ray diffractometer D/MAX-2200, CuK_α radiation]. A scanning electron microscope was employed to investigate the changes in the surface morphology of the nanocomposites with different hydroxyapatite/TiO_2 concentrations. The elemental compositions of the films were evaluated by energy dispersive X-ray analysis. The synthesized samples were also characterized by FTIR [Nicolet avatar 330 series].

RESULTS AND DISCUSSION

X-Ray diffraction anlaysis: The XRD patterns of the hydroxyapatite/TiO_2 nanocomposites films prepared with different concentrations are shown in Fig. 1 (patterns A-E). The characteristic diffraction peaks were found to be in good agreement with hydroxyapatite (JCPDS card #09-0432). The characteristic peaks of hexagonal hydroxyapatite (pattern A) at 2θ values of 25.89, 31.77, 32.87, 46.67 and 48.07 show the highly crystalline apatite peaks. The XRD patterns of 50 and 80 vol % TiO_2 (patterns B and C) indicate a steady peak shift with increasing TiO_2 concentrations and in composites with more than 50 vol % of TiO_2, a domination of TiO_2 phase is observed. This confirms, initially there was a small inclusion of TiO_2 in hydroxyapatite (Ti^{2+} may replace few of the Ca^{2+}). Excess, TiO_2 nanoparticles deposited on the surface of the substrate behaves as a matrix for hydroxyapatite growth. Because no other new peaks other than hydroxyapatite or TiO_2 was observed in the XRD pattern. Addition of 20 vol % TiO_2 to hydroxyapatite (pattern D) shows almost similar diffraction pattern like pure hydroxyapatite with a small reduction in the intensity of hydroxyapatite peaks (25.89-25.79). However on closer examination the peaks were found to have shifted towards lower angles, confirming the TiO_2 inclusion in hydroxyapatite. All the XRD patterns confirm the high chemical and thermal stability of the hydroxyapatite/TiO_2 nanocomposites even after annealing at 500 ºC. Fig. 1 (pattern E) shows the pure TiO_2 with the characteristic anatase phase (JCPDS card #21-1272).

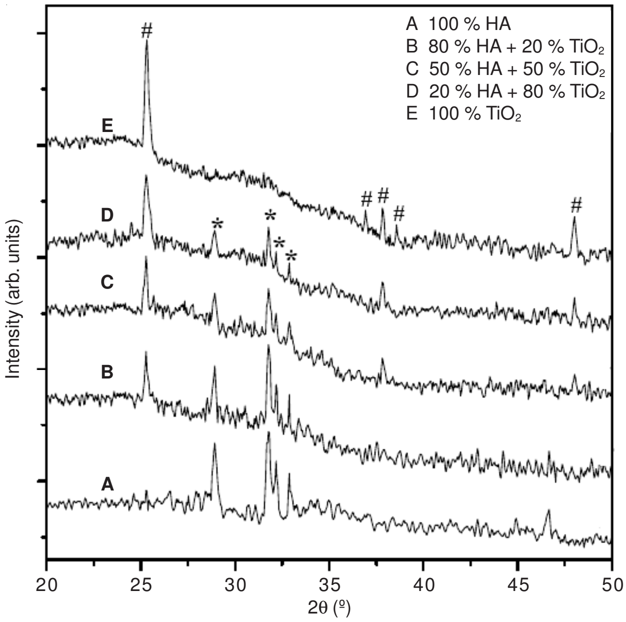
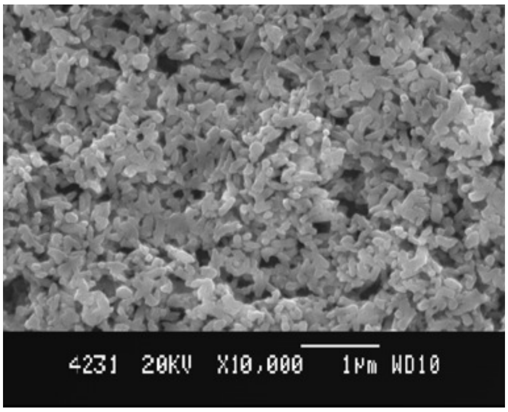
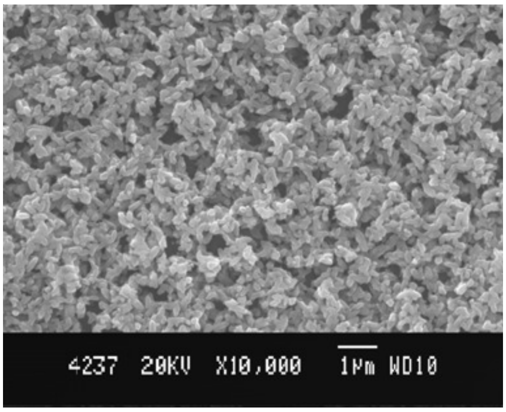


Fig. 1. XRD pattern of hydroxyapatite/TiO_2 nanocomposite thin films

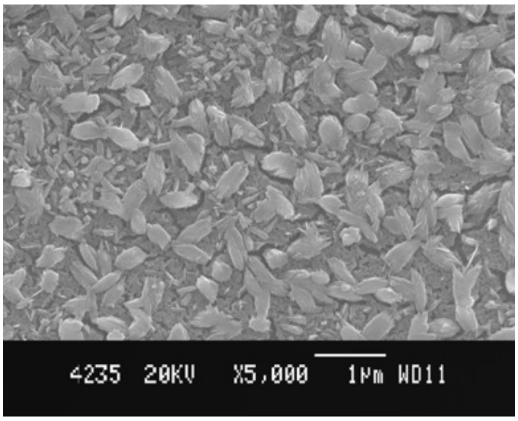
Morphological analysis: The surface morphology of the TiO_2 thin films coated on glass substrates is shown in Fig. 2(a-e). The microstructure consists of well developed stems and microspores forming a highly interconnected porous network. Fig. 2b shows the SEM image of 20 vol % TiO_2 added hydroxyapatite thin film, which indicates changes in the morphology of the nanocomposites. As the percentage of TiO_2 is further increased the formation of plate like structure is clearly seen. Fig. 2c shows the 50 % addition of TiO_2 to hydroxyapatite. The size of the nanostructure is less than 500 nm. The morphology of the 80 vol % TiO_2/hydroxyapatite thin films (Fig. 2d) shows almost plain microstructure with very few hydroxyapatite nanoparticles grown on the TiO_2 surface. The image of pure TiO_2 coating (Fig. 2e) shows uniform and crack free coating.



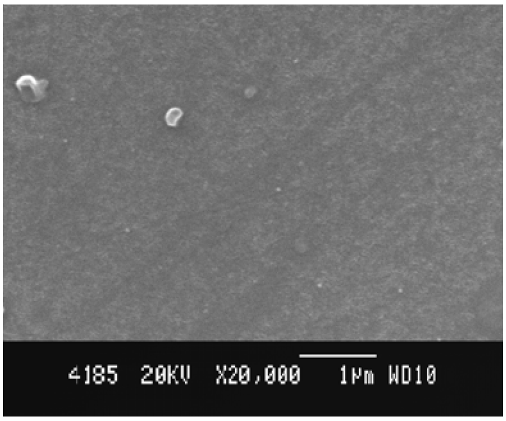
(a) Pure hydroxyapatite



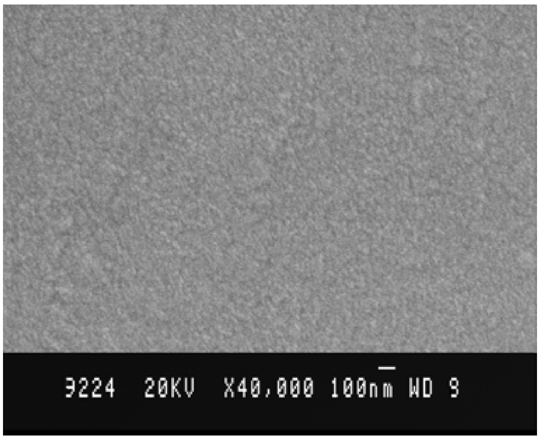
(b). 20 vol % TiO_2



(c) 50 vol % TiO_2



(d) 80 vol % TiO_2

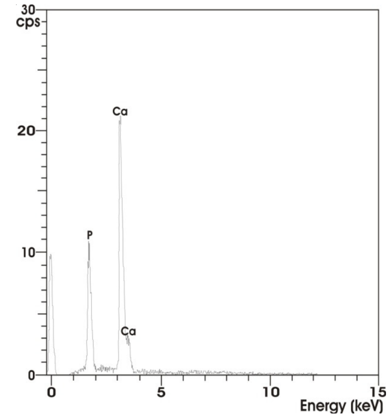


(e) Pure TiO_2

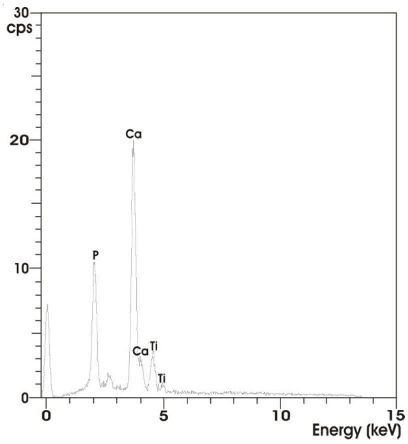
Fig. 2. SEM images of hydroxyapatite/TiO_2 nanocomposite films

The above results confirm that the addition of TiO_2 plays a crucial role in determining the morphology and grain size of hydroxyapatite. It could be observed that, the increase in TiO_2 concentration reduces the size of hydroxyapatite nanoparticles in the coatings[9]. The TiO_2 used in these coatings facilitates complete adhesion of the coatings with the glass substrate and also functions as a nucleating agent during the annealing of the hydroxyapatite/TiO_2 composite film at 500 ºC. The microstructure analysis shows that TiO_2 forms as a layer on the glass substrate and acts like a crystallized matrix for the growth of hydroxyapatite nano particles. In general, the presence of crystallized TiO_2 anatase phase favours the ordering of the randomly distributed Ca and P ions thus leading to the formation of an apatite structure. It has also been reported that the anatase phase of TiO_2 favours the nucleation and growth of apatite hydroxyapatite, rather than the rutile phase. This might be because of the better lattice match between the anatase form of TiO_2 and hydroxyapatite[10].

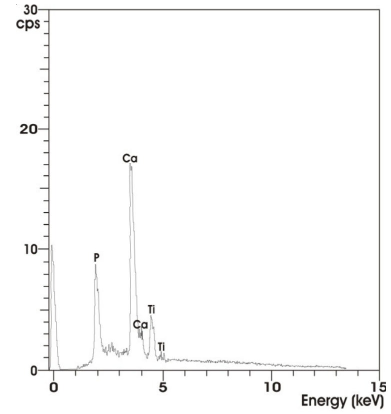
EDAX analysis: The energy dispersive spectroscopy profile of the samples in Fig. 3(A-E) reveal that the concentration of Ca/P ratio for the hydroxyapatite containing samples is in the range of 1.7-1.92 which is close to the hydroxyapatite stoichimetry of 1.67. For the prepared film from 100 % hydroxyapatite sol, high concentrations of only Ca and P is present. Addition of TiO_2 sol to HA decreased both the Ca and P concentrations in the films. Fig. 3c shows the EDAX pattern for 50 % TiO_2 added hydroxyapatite coating confirming the presence of Ti, Ca, P and O. Since no other elements are observed from



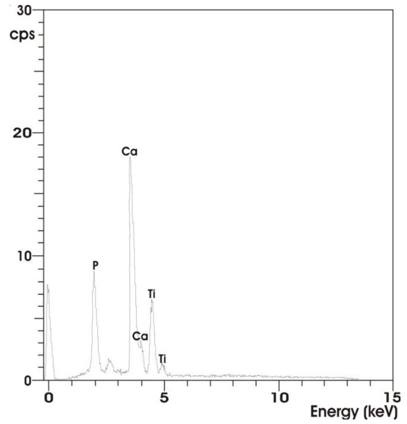
(a) Pure hydroxyapatite



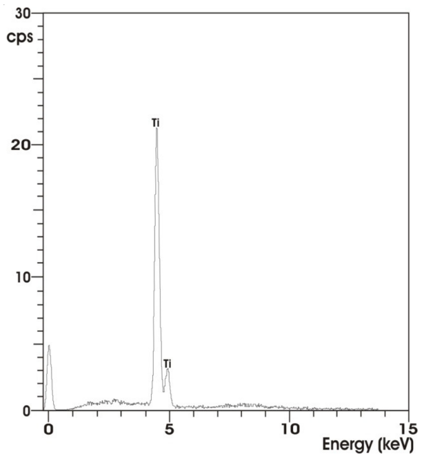
(b) 20 vol % TiO_2



(c) 50 vol % TiO_2



(d) 80 vol % TiO_2



(e) Pure TiO_2

Fig. 3. EDAX pattern of hydroxyapatite/TiO_2 nano composite films

the EDAX analysis it could be understood that the nanocomposites comprise only of titania and hydroxyapatite.

FTIR analysis: FTIR spectra of the hydroxyapatite/Titania composites are shown in Fig. 4 (patterns A-E). The peak labelled at 3570 cm^{-1} is assigned to the stretching mode of hydroxyl (OH^-) group in hydroxyapatite. The stretching vibration bands of PO_4^{3-} labeled at 958 and 1091 cm^{-1} are observed in the figure (patterns A-D). However, in the composite coating, the resolution diminishes, which may be due to the relative content of the vibration mode group. The peaks labelled at 569 and 600 cm^{-1} indicate the bending mode PO_4^{3-}.

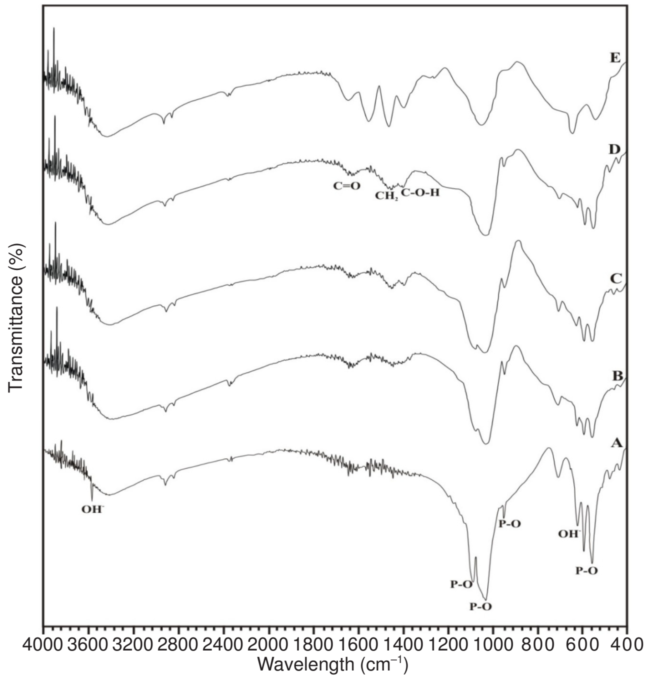


Fig. 4. FTIR spectra of hydroxyapatite/TiO_2 composites

Conclusion

Nanostructured composite thin films of hydroxyapatite/TiO_2 with different concentrations of TiO_2 have been successfully fabricated by sol-gel dip coating process. The structural analysis confirms the formation of nanocomposites and the relative change in peak intensities with increase in TiO_2

concentrations. The analysis using SEM shows that the morphology of the composite films varies with the different ratios of hydroxyapatite and TiO_2. The addition of TiO_2 promotes the adhesion of hydroxyapatite film on the glass substrate and also reduces the roughness of the coating. The FTIR studies confirmed the presence of hydroxyl bands at 3570 cm^{-1} and the stretching vibration bands of PO_4^{3-} at 958 and 1091 cm^{-1}. In the present study thus an attempt was made to establish the involvement of a chemical component in the adhesion of TiO_2-hydroxyapatite coatings to that of pure hydroxyapatite coatings and the results indicate a material with a very promising potential for orthopaedic and dental implant applications.

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