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Photocatalytic performance and antimicrobial activities of HAp-TiO_2 nanocomposite thin films by sol-gel method

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ABSTRACT

Hydroxyapatite/titanium dioxide composite thin films of different dipping cycle have been prepared by sol-gel processes. The morphology, chemical compositions and structures of the thin films were characterized by scanning electron microscope (SEM), Energy dispersive X-ray analysis (EDX). The crystalline phase and structure of the thin film nanocomposites were determined by XRD. The crystalline sizes of the composites were estimated in the range from 10 nm to 25 nm. The peak intensity of anatase phase increases with the increase of TiO_2 concentration in the HAp/TiO_2 composite there is no other impurity phases present in state. From the XRD peaks at $2\theta = 31.724°$, 31.706°, 31.731°, and 31.615° are the prominent characteristic peaks of HAp hexagonal phase. The addition of TiO_2 clearly showed the development of rutile peaks at $2\theta = 66.248°$, 66.226°, 66.253°, and 66.146° which are the prominent characteristics peak of TiO_2 rutile phases. The microstructural studies confirm that the HAp is embedded in the titania matrix. EDX analysis confirmed the presence of Ca, P, Ti and O respectively. The IR spectroscopy was performed on HAp/TiO_2 thin films deposited on glass substrate. The stretching and vibrational properties of composites were reported the broad and medium peaks where observed at 440, 705 cm^{-1} which also indicates the titania with rutile phase. The optical absorbance coefficient of a semiconductor close to the band edge can be expressed by the optical bandgap of HAp/TiO_2 composite films of 4, 6 and 8 dipping cycle is 3.8 eV, 4.0 eV and 4.1 eV respectively, from the literature the optical bandgap energy of HAp is 5.3 eV and TiO_2 is 3.2 eV In our present study, significantly mid bandgap values have been observed. The antimicrobial activity test results showed that the composite films exhibited good inhibition on Gram positive and Gram negative bacteria.

1. Introduction

Several paradigm shifts have been takes place in different areas such as electronics, robotics, medicine and surgery by the advent of nanocomposite materials. To some extent, the field of medicine and surgery is the most important area because it is related to human's health [31]. In this case biomaterials play a vital role. Among different categories of biomaterials, hydroxyapatite (HAp), has received an extensive attention for its use as bone filler and implant material due to its excellent biocompatibility, close chemical and crystallographic structure with the mineral phase of natural bone [1,10,23,27,37]. Hydroxyapatite is not only a main component of hard tissue, such as bone and teeth, but a material applied for bioceramics and adsorbents because it has an excellent affinity to biomaterials such as proteins [11,17]. The mechanical properties of HAp are poor, especially in wet environment, alarming their limitations for the use in heavy loaded implants such as artificial bones or teeth. Thus, regardless of the favorable biological properties, the

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poor mechanical properties of the HAp bioceramics can lead to an instability and unsatisfactory performance of the implant or scaffold in the presence of body fluids and under local loadings [7,38]. To overcome these mechanical limitations is to use bioactive HAp as ceramic/metal composites so as to achieve both the necessary mechanical strength and bioactive properties [28]. Such composites are expected to have improved mechanical strength compared to pure ceramic. It has been reported that titania and HAp represents a good combination for functionally graded materials providing a gradient of bioactivity and good mechanical properties [26]. In addition to the bioactive properties, hydroxyapatite has great sorption properties, which are of great importance for both environmental process and industrial purpose including fertilizer production, water purification, and degradation of pollutants and fabrication of biocompatible ceramics [13,14]. The phenomena of photo induced electronic excitation in HAp is similar to the phenomena of photocatalysis in TiO_2, which is well established material used for the degradation of organic molecule [15,33]. Titanium dioxide (TiO_2) has been investigated extensively for the killing or growth inhibition of bacteria [8]. Hence a combination of HAp and TiO_2 composite has the ability to absorb and decompose bacteria and organic materials and is considered to be good in antibacterial applications and environmental purifications [16,25]. Recently (Jahida et al., 2015) was reported that the introduction of the titania film, significantly improve the bonding strength of the HAp layer to substrate. In the field of biomedical, many failures in the implantation are may be due to the formation of microbes in the implanted site. The usage of inorganic antibacterial agents has attracted interest for the control of microbes. If the implant material has the capability of antimicrobial within them, then the problem of failure will be reduced. Moreover, microbes which cause a wide variety of infections in human and other animals can spread through common place like bathroom tiles, doorknobs, packing materials etc. can be controlled by the antimicrobial materials and coatings. The present work is mainly focused on the study of structural, optical properties and antimicrobial activity of the hydroxyapatite/TiO_2 composites thin films prepared by sol-gel technique. Several techniques for production of nanostructured thin film have been proposed. Among these, the sol-gel is a relatively easy technique for preparing thin films with complex structure [6]. There have been many investigations of films derived using sol-gel method, owing to its advantages, which includes low processing temperature, homogeneity, the possibility of coating substrate with large area and low cost [35]. The effect of different amount of titania additive on HAp was investigated on microstructure of HAp/TiO_2 composites by scanning electron microscope (SEM). X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and energy dispersive x-ray analysis (EDX) were also employed to characterize the crystal structure and chemical composition of the sample. The antimicrobial activity was tested by disc diffusion method against pathogenic organisms such as *Bacillus* spp. and *E.coli.*

2. Experimental details

2.1. Preparation of HAp/TiO_2 composite thin film

Titanium (IV) isopropoxide [$C_{12}H_{28}O_4Ti$] (TTIP) of purity 99.99% was used as a source material for Titanium [Ti] and was purchased from Sigma Aldrich. Ethanol and double distilled water (dH_2O) were used as solvents and acetic acid was used as a stabilizing agent. The ethanol, acetic acid and orthophosphoric acid [H_3PO_4] were obtained from E-Merck. Microscopic glass slides (Borosilicate glass pk72) of the dimensions 75 mm × 25 mm × 1 mm were used as substrates. The substrates were washed with soap solution for 5 min and subsequently kept in the hot chromic acid at 40 °C for 20 min. Finally the substrates were cleaned ultrasonically and washed with distilled water. For getting HAp precursor solution, 0.05 M solution of calcium acetate [$Ca(C_2H_3O_2)_2$] was prepared by dissolving the appropriate amount of calcium acetate salt mixed with 100 ml of solvent (75 ml of double distilled water and 25 ml of ethanol) and stirred for 5 h under vigorous conditions at room temperature to obtain a sol-gel solution and then 0.03 M of orthophosphoric acid [H_3PO_4] is added drop by drop in above prepared sol-gel solution. Finally the transparent HAp solution is formed after stirred in 5 h. During the preparation of HAp solution the pH of the solution is maintained at 10.5 by adding the aqueous ammonia.

The TiO_2 colloidal solution is prepared by hydrolysis of titanium (IV) isopropoxide (TTIP) in a typical process, 1 M of titanium (IV) isopropoxide is mixed with 4 M of acetic acid in the same resultant solution. Double distilled water and 0.1 M of HCl were mixed together and stirred vigorously for about 1hr at room temperature to obtain the final transparent solution. HAp/TiO_2 nanocomposite solution is mixed together with proportion ratio of (3:1) 75 ml of HAp solution and 25 ml of TiO_2 solution. The prepared HAp/TiO_2 precursor solution was used to prepare the composite thin films by varying the dipping cycle. Microscopic glass substrates with appropriate dimensions were dipped in the resultant sol-gel solution. Each substrate was immersed in to the solution in the dipping rate of 20 s; similarly dipping cycle of 4, 6 and 8 dip film is coated on substrates. Subsequently the dipped glass substrates were baked at 100 °C for 10 min and then allowed to reach ambient temperature. Then the baked films were annealed at 500 °C for 1 h in a muffle furnace at a constant heating rate under an air atmosphere.

2.2. Characterization studies

The crystalline phase and structure of the thin film nanocomposites were determined by using Philips X' PERT-PRO powder x-ray diffractometer ($2\theta = 10°$ - $80°$, $CuK_\alpha = 1.540$ Å) with the range of the diffraction angle 2θ values are recorded between the ranges 20°–80° The absorption spectra of the thin film samples (4, 6 and 8 dip) were recorded in the wavelength of range 200 nm–900 nm using Thermofischer Helios Alfa UV–Vis-NIR spectrometer Thermofischer Helios Alfa. The vibrational properties of the HAp/TiO_2 composite thin films were analyzed by Fourier transform infrared spectroscopy (FTIR) by using Nicolet 740FTIR spectrometer. The morphology and microstructure were examined using field emission scanning electron microscopy (FESEM) performed on a (Philips CM12) with an acceleration voltage of 20 kV. The energy dispersive spectroscopy (EDS) (IH-300X) analysis was performed at several points in the FESEM arrangement. The HAp/TiO_2 composite thin films were tested for antimicrobial activity by disc diffusion method against pathogenic organisms such as *E.coli.* and *Bacillus* spp. The pure cultures of organisms were sub-cultured on nutrient broth at 35 °C employing a rotary shaker at 300 rpm. Loop full isolated subculture swabbed on Mueller Hinton agar plate. The pre culture plate was prepared by standard method. After solidification of the agar plate, different types of test pathogens were swabbed in each of the agar plate using sterile cotton buds and labeled clearly. The plates were then supplemented with different composite thin films and incubated at 37 °C for 24 h of incubation to observe the zone of inhibition.

2.3. Photocatalytic performance test

A small amount of HAp/TiO_2 was added to double-deionized water and the mixture was sonicated for 20 min at room temperature to disperse the solid catalyst particles before the addition of an appropriate amount of the 20 mL. The catalyst-loaded RhB solution was illuminated under UV, visible, and UV+visible light for 60 min, respectively, and sampling was done at 15 min intervals. At