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Mechanical and photocatalytic properties of hydroxyapatite/titania nanocomposites prepared by combined high gravity and hydrothermal process

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ABSTRACT

Hydroxyapatite/titania nanocomposites of different ratios have been successfully synthesized by combined high gravity and hydrothermal methods. SEM and TEM observations showed that small spheres of TiO_2, identified as anatase crystals of 10–15 nm, were deposited on HAp rod-like crystals. EDAX analysis confirmed the presence of Ca, P, Ti and O. X-ray diffraction patterns indicated the presence of hydroxyapatite and anatase phase. More number of anatase peaks appeared in the XRD patterns with higher colloidal concentration of TiO_2 in the HAp/TiO_2 compound. Mechanical stability of the HAp/TiO_2 nanocomposites was determined by reinforcing them with high molecular weight polyethylene (HMWPE) and the tensile strength of the samples was analyzed. Photocatalytic activity of the HAp/TiO_2 particles was examined by decomposition of methyl orange (MO). The results showed that photocatalytic properties of HAp/TiO_2 composites are more effective than that of individual HAp and TiO_2 which implied that the HAp improved the photocatalytic activity of well known photocatalyst TiO_2.

1. Introduction

Increasing demands for smarter and smaller products call for the development of multiphase and multifunctional materials. Significant progress in ‘‘nanochemistry” has given birth to a newly emerging area called ‘‘nanohybrid” or ‘‘nanocomposite” materials, which results from the tuning of molecular level interactions of dissimilar inorganic components to form new, unique functional materials with improved properties [1]. In recent years, with the growing necessity for biomaterials, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, abbreviated as HAp, has received 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 [2]. Hydroxyapatite is not only a main component of hard tissues, such as bones and teeth, but a material applied for bioceramics and adsorbents because it has an excellent affinity to biomaterials such as proteins [3]. Studies have shown that the properties of the ceramics could be improved remarkably by making one dimensional (1-D) nanoscale building blocks such as nanorods, nanofibers and nanotubes [4,5]. However, the synthesis of HAp particles in the nanometric scale is very difficult due to their tendency to agglomerate.

The mechanical properties of HAp are poor, especially in wet environment, alarming their limitations for use in heavy-loaded implants, such as artificial bones or teeth. Thus, regardless of their favorable biological properties, the poor mechanical properties of HAp bioceramics can lead to instability and unsatisfactory performance of the implant or scaffold in the presence of body fluids and under local loading [6,7]. The best way 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 [8]. Such composites are expected to have improved mechanical properties compared to pure ceramics, and better structural integrity and flexibility than brittle ceramics. It has been reported that titania and HAp represent a good combination for functionally graded materials providing a gradient of bioactivity and good mechanical properties [9]. In a similar manner, polymer/ceramic composites scaffolds mimic the natural bone and could provide reinforced porous structures with enhanced bioactivity, mechanical stability and controlled resorption rates [10]. The combination of HAp/TiO_2/polymer further increases the mechanical behaviour to some extent.

In addition to the bioactive properties, HAp has great sorption properties, which are of great importance for both environmental processes and various industrial purposes including fertilizer production, water purification, degradation of pollutants and fabrication of biocompatible ceramics [11]. The phenomena of photo-induced electronic excitation in HAp is similar to the phenomena

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of photocatalysis in TiO_2, which is a well established material used for the degradation of organic molecules [12]. Hence, a combination of HAp and TiO_2 to form a composite has the ability to adsorb and decompose bacteria and organic materials and is considered to be good in antibacterial applications and environmental purifications and also for photocatalytic decomposition of biomaterials, such as proteins and lipids [13–15].

In our present work, HAp/TiO_2 nanocomposite has been successfully synthesized by combined high gravity and hydrothermal treatment of colloidal HAp and TiO_2 solutions. In order to overcome the problem of agglomeration of HAp nanoparticles in the absence of any external agents, we made an attempt to synthesize the particles using the high gravity method and then treat them with hydrothermal method. In this process, we could achieve agglomeration free pristine HAp and HAp/TiO_2 nanocomposites with homogeneous structure. The details of the high gravity method is explained elaborately. The morphological changes in the composite due to the addition of the TiO_2 were analyzed in detail. Further, we studied how these changes influence the mechanical property as well as the photocatalytic activity. We have also made an attempt to develop a mechanically stable nanocomposite and novel photocatalyst with a high affinity to biomaterials by modifying HAp particles with TiO_2.

2. Experimental details

2.1. Principle of rotating packed bed (RPB)

The HAp/TiO_2 nanocomposites were prepared by combined high gravity and hydrothermal methods. A rotating packed bed (RPB) arrangement is the key part of the high gravity instrument. The schematic structure of RPB is illustrated in Fig. 1. RPB has a packed rotator which is placed inside a stationary shell and rotates with a speed of several hundreds to thousands of revolutions per minute. Solutions are introduced into the eye space of the rotator from the inlet and sprayed onto the inside edge of the rotator through a slotted distributor. The flow rates of the solutions are controlled by the flow meter. The solution in the bed flows in the radial direction from the inside to outside edge under centrifugal force and finally leaves RPB via the outlet. The basic principle of RPB is to create a high-gravity environment via the action of centrifugal force, where mass transfer and micro-mixing can be intensified tremendously. Solutions going through the packing is spread or split into micro or nano droplets, threads or thin films under the high-gravity environment within the RPB, which is of the order of several hundred or even several thousand times larger than the gravitational acceleration of the earth.

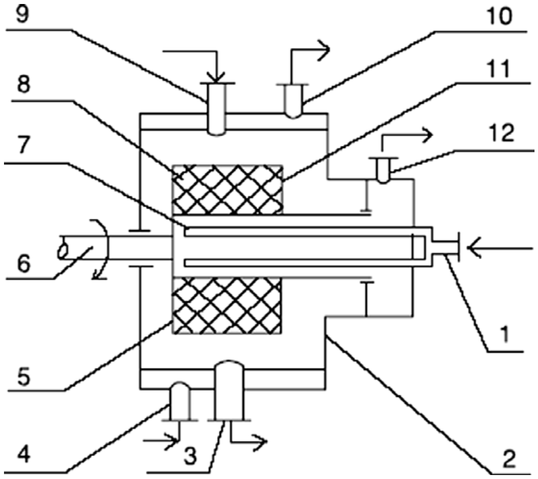

Fig. 1. Schematic diagram of RPB: (1) liquid inlet, (2) shell, (3) liquid outlet, (4) water inlet, (5) rotor, (6) shaft, (7) liquid distributor, (8) packing, (9) gas inlet, (10) water outlet, (11) seal and (12) gas outlet.

2.2. Synthesis of HAp colloidal solution

In a typical synthesis procedure, calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) were used as calcium and phosphate sources, respectively. The HAp was prepared by taking the above compounds separately and mixed with de-ionized water with the molar ratio of 1:0.6 to maintain the Ca/P ratio 1.67 which is the stoichiometric molar ratio of HAp. The pH of the phosphate solution was increased to 9 by adding ammonium hydroxide (30%). The prepared Ca and P solutions were pumped through the two different solution inlets into the RPB of the high gravity setup where both solutions were mixed and reacted with each other to form HAp nanoparticles. The flow rate of Ca and P solutions was controlled by using the liquid flow meter. The mixed solution was re-pumped from the outlet into the RPB and mixed thoroughly with an rpm of 1500 and the process was repeated for two times.

2.3. Synthesis of TiO_2 colloidal solution

The TiO_2 colloidal solution was prepared by hydrolysis of titanium tetra isopropoxide (TTIP) (Aldrich chemicals, USA). In a typical process, 1 M of titanium tetra isopropoxide was mixed together with 4 M of acetic acid. The resultant solution is mixed with 10 M of double distilled water and the solution was stirred vigorously for 1 h to obtain a clear solution. After an aging period of 24 h, the solution was kept in an oven at 70 °C for 12 h to obtain $Ti(OH)_4$ colloidal solution.

2.4. Synthesis of HAp /TiO_2 nanocomposite

HAp/TiO_2 nanocomposite was prepared from HAp and $Ti(OH)_4$ colloidal solutions by pumping them through two different solution inlets into the RPB. The mixed HAp/TiO_2 solution with different TiO_2 proportion of 0,10, 20, 40, 60 and 100 wt.% was transferred to the Teflon beaker of the stainless steal autoclaves and placed in an oven at 180 °C for 12 h and then cooled to room temperature naturally. The final precipitate was washed several times with distilled water and dried at 100 °C over night. The samples were calcinated at 600 °C for 1 h before further characterization.

2.5. Preparation of HAp/TiO_2/HMWPE nanocomposite

The mechanical stability of the composite was analyzed by reinforcing it with high molecular weight polyethylene. Nanocomposites of HAp/TiO_2 prepared by combined high gravity and hydrothermal method was mixed with HMWPE. Before mixing, HMWPE and the nanocomposites were dried in an oven at 120 °C for 1 h and cooled down to room temperature to remove the moisture contents. Ten percent of each nanocomposites were mixed with the HMWPE separately. The blending was carried out in a micro compounder (HAAKE MiniLab II) with the mixing temperature of 180 °C. A mixing time of 20 min was fixed for all the samples and the rotor speed at 80 rpm. A piston injection moulding system (HAAKE MiniJet 557-2270) was used for preparing specimen to study the mechanical behaviour.